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Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, & Liquefied Nat. Gas Plants

Radian Corporation

Prepared For
Industrial Environmental Research Lab.

November 1975

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ENVIRONMENTAL PROBLEM DEFINITION FOR PETROLEUM REFINERIES, SYNTHETIC NATURAL GAS PLANTS, AND LIQUEFIED NATURAL GAS PLANTS

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ENVIRONMENTAL PROBLEM DEFINITION FOR PETROLEUM REFINERIES, SYNTHETIC NATURAL GAS PLANTS, AND LIQUEFIED NATURAL GAS PLANTS

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ABSTRACT

Information in this report was compiled for the purpose of providing the Environmental Protection Agency with technical support in the area of total environmental problem definition for petroleum refineries, synthetic natural gas (SNG) plants, and liquefied natural gas (LNG) plants.

Process descriptions are presented for each plant. Where applicable, comparisions to other types of energy conversion plants are made. Potential ambient air emissions, liquid effluents, and solid wastes are identified and the status of monitoring methods and control techniques for these emissions and wastes are discussed.

The problems involved with the siting of new plants because of the impact of these emissions and wastes are considered. Areas where research and development can be usefully applied to these environmental problems are identified.

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1.0 INTRODUCTION

1.1 Project Objectives

The objective of this report is to provide technical information on the total environmental problem definition with respect to petroleum refineries, synthetic natural gas (SNG) plants based on conventional liquid feedstocks, and liquefied natural gas (LNG) plants. This report includes the following major elements:

(1) A review of the present technological position (state of the art) of petroleum refineries, SNG plants, and LNG plants and their relationship to synthetic fuel processes

(2) Definition of modules representing typical refineries (fuel oil producing and gasoline producing), SNG plants, and LNG plants.

(3) Identification of emissions and effluents from these modules in terms of the media impacted (air, water, solid) and the quantity and composition of effluent streams.

(4) A review of effluent monitoring methods which could be applied to the projected effluent streams.

(5) A review and comparision of control methods which may be employed at refineries, SNG plants, and LNG plants.

(6) Identification of plant impact and siting problems.

(7) Identification of priority work areas for research and development activities.

The work performed in this study divides into essentially two areas: (1) the identification of emissions and emission sources for the three technologies and (2) the evaluation of environmental requirements resulting from these emissions in terms of monitoring methods, control techniques, plant impact and siting problems, and areas for research and development. Sections 2.0 and 3.0 of this report examine the refinery, SNG, and LNG technologies and establish the emissions associated with these industries, while Sections 4.0-7.0 address the various environmental aspects and problems resulting from these emissions. Only criteria pollutants such as particulates, SO_x, CO, NO_x, and HC are quantified in Section 3.0; however, Sections 4.0-7.0 are more qualitative in nature, covering potential pollutants such as trace elements and trace organics.

1.2 Modular Concept

A modular approach is utilized in this analysis. Since the initial step in establishing a representative module for an industry involves a review of the technological position of that industry, state of the art descriptions for the petroleum refining, SNG, and LNG industries are presented in Section 2.0. Various classifications and services within each technology are reviewed. Processing options and alternatives are considered, and typical processes and processing sequences are identified for each technology. Also included in this section is a comparision of the refining, SNG, and LNG industries with new energy technologies (coal gasification, coal liquefaction, and shale oil production). The purpose of this comparison is to identify areas of the new energy systems to which the information generated in this study might apply.

Utilizing typical processing sequences developed in Section 2.0, process modules are derived in Section 3.0. The modules presented in this report are for a fuel oil refinery, gasoline refinery, SNG plant, and LNG plant. Due to the many processing alternatives possible in petroleum refinery operations, two refinery modules are presented, each representing a different product emphasis (gasoline and fuel oil). Module flow rates are determined assuming typical size commercial plant operation and utilizing specific process yield data. After each module is established in terms of processes, flow rates, and energy or fuel demand, the emission sources and emissions for that module are presented in terms of source and media impacted. Air emissions, water effluents and solid wastes are considered in this study. Also included in Section 3.0 is a comparision of the emissions resulting from the different modules on a common Btu output basis.

1.3 Summary of Environmental Problems

Using the modules given in the previous sections, environmental problem areas can be determined for each of the energy conversion plants. Once the problem areas have been recognized, Section 4.0 and Section 5.0 can be used to define specific monitoring and emission control techniques which can be applied to each of the problem areas.

1.3.1 Fuel Oil Refinery

Air Emissions

The major air pollution sources for particulates, SO_x, CO, and NO_x within the fuel oil refinery module are the process heaters and boilers. These sources include the following:

- crude distillation,
- gas oil hydrotreater,
- naphtha hydrotreater,
- heavy naphtha reformer,
- C_5/C_6 isomerization,
- propane deasphalting unit,
- tail gas treating plant, and
- light ends recovery.

The heaters and boilers used for these units are fired by refinery fuel gas, heavy fuel oil, or coke gas from the flexicoker.

The major source of hydrocarbon emissions are general fugitive emissions throughout the refinery. The exact sources are difficult to identify and even harder to quantify. The number used as the overall fugitive emission factor in the refinery module (0.1 wt% of the throughput) is at best a rough estimation.

Another major source of hydrocarbons is the crude and petroleum products storage tanks. With the increasing value of hydrocarbons, more effective and costly systems for controlling storage tank losses are becoming economically feasible.

Another primary pollution source is the tail gas from the acid gas treating plant. New methods of controlling emissions can remove up to 99.9% of the hydrogen sulfide originally introduced to the acid gas plant. However, due to the relatively large volume of the acid gas stream, the total emission of SO_x to the atmosphere after treating is still very substantial.

A final air emission source within the fuel oil refinery module is the sludge incinerator. Other methods of handling the sludge such as landfilling will reduce or eliminate the air pollution from this source.

Water Effluents

The major sources of contaminated water within the fuel oil refinery are the following:

- sour water stripper condensate,
- contaminated process water,
- cooling tower blowdown,
- caustic wash water, and
- desalter water.

Other potential contaminated water sources are oily process area storm water, oily cleaning water, and oily water from a ship's ballast (if located near a docking facility). The combined wastewater from these sources is treated in a wastewater treating plant. Presently, many alternatives exist for treating wastewater and a treating facility can be designed to handle many specific wastewater problems.

Uncontaminated wastewater is also generated within the refinery. This water is handled separately from the contaminated water by a segregated wastewater system. The uncontaminated water along with treated process wastewater is retained in a holding pond for a certain period of time before final discharge to the local environment.

Solid Wastes

Sources of solid wastes within the fuel oil refinery module include:

- entrained solids in the crude,
- silt from surface drainage,
- silt from water supply,
- corrosion products from process units and sewer systems,
- solids from maintenance and cleaning operations,
- sludge from water treatment facilities (or ash from the sludge incinerator), and
- spent catalyst.

Being inert and acceptable for landfill, the generated solid wastes do not usually present an environmental problem.

1.3.2 Gasoline Refinery Module

Air Emissions

The major air pollution sources for particulates, SO_x, CO, and NO_x within the gasoline refinery module are the process heaters and boilers. These sources include all those indicated for the fuel oil refinery in addition to a middle distillate hydrotreater, a heavy hydrocrackate reformer, and alkylation plant, and a hydrogen plant. Once again the fuels which are used include refinery fuel gas, heavy fuel oil, and coke gas from the flexicoker along with naphtha which is combusted in the hydrogen plant.

Major sources of hydrocarbon emissions within the gasoline refinery are the same as the fuel oil refinery. The majority of hydrocarbon emissions results from general fugitive emissions and from crude and petroleum product storage tanks. Also, as in the fuel oil refinery, a primary emitter of SO_x is the acid gas treating plant.

A unique air pollution source within the gasoline refinery module is the fluidized catalytic cracking unit (FCCU). Uncontrolled the FCCU would be a major source of particulates, SO_x, and carbon monoxide. Controls as described in Section 5.1 have, however, greatly reduced this problem.

Water Effluents

The water problems involved with the gasoline refinery module are the same as the fuel oil refinery module.

Solid Wastes

The solid wastes generated in the gasoline refinery module are the same as the fuel oil refinery module.

1.3.3 Liquefied Natural Gas (LNG) Plants: Peak-Shaving and Base Load

Air Emissions

The major air pollution sources for particulates, SO_x, CO, and NO_x within the LNG modules are natural gas-fired heaters in the boiler units and the regasifiers. A heater is also needed to regenerate the molecular sieve bed but the heat load is small relative to the boiler and regasifier, and thus the emissions are considered negligible.

The major source of hydrocarbon emissions are fugitive emissions from all of the processing units. The same emission factor used in the refineries is used here to determine the fugitive losses.

If a glycol unit is being used to dehydrate the natural gas before liquefaction, then there will be a continuous discharge of glycol vapor (as triethylene glycol) along with the water vapor. About 0.05 gallons of the glycol is emitted per million standard cubic feet of natural gas processed.

Water Effluents

The majority of the wastewater effluent generated within the LNG module is from the acid and caustic wash water streams used for the demineralizer regeneration. This stream is very small and can be handled by a small holding pond or by direct discharge into a municipal sewage system.

Solid Wastes

There are no significant solid wastes generated within the LNG module.

1.3.4 Synthetic Natural Gas (SNG) Plant

Air Emissions

The major sources of particulates, SO_x, carbon monoxide, and NO_x within the SNG module are process heaters and boilers. These sources include the following:

- preheaters,
- super heater,
- steam boiler,
- Benfield CO_2 removal system, and
- glycol dehydration unit.

All of these units are fired with low sulfur naphtha.

The Benfield CO_2 removal system is a major source of hydrocarbon emissions from the LNG module. Although the concentration of hydrocarbons (mainly methane) is small in the vented CO_2 stream, the large volume of vented gas makes the total amount of hydrocarbons emitted very substantial. The other sources of hydrocarbon emissions are fugitive emissions from all the processing units and emissions from naphtha storage tanks. Additional hydrocarbons are emitted in the form of glycol from the glycol dehydration unit venting system.

Water Effluents

The wastewater from the SNG module consists of the acid and caustic wash water streams used for the demineralizer regeneration, the cooling system and boiler blowdown streams, and the waste solution from the Benfield system. The total stream flow is small and can be handled by a small holding pond or by direct discharge into a municipal sewage system.

Solid Wastes

There are no daily discharges of solid wastes from an SNG plant. Disposal of spent catalysts occur periodically but do not pose an environmental problem because the catalyst is inert and acceptable for landfilling.

1.4 Comparison of Module Emissions

In the following subsections the emission rates will be related to the specific module charge capacity. This approach is used in order to present the emission impact of a typical size plant for the specific industry and hence facilitate its environmental assessment for each technology. In this subsection all of the modules are adjusted to a 10^{12} Btu/day output of primary product. This adjustment is made in order to present the different module emissions on a common basis and provide a convenient comparison of the emission impact of the various technologies. This comparison is presented in Table 1.4-1. The large hydrocarbon emissions that result from these modules are primarily a result of fugitive losses (assumed 0.1 wt% of throughput).

1.5 Evaluation of Environmental Requirements

After the emissions and emission sources have been identified, various environmental control requirements and problems are addressed. Applicable emission and effluent monitoring methods are presented in Section 4.0. Differences in ambient air sampling and effluent sampling are discussed, and monitoring data such as accuracy and costs per sample are presented. Problem areas associated with monitoring technology are identified and gaps in technology noted.

Following the discussion of monitoring methods, emission control techniques are addressed in Section 5.0. Potential control methods are described and alternative control methods are compared. Problem areas such as fugitive and toxic chemical emissions are discussed. Control methods capable of the most pollutant reduction are identified and any techniques having potential for near zero emissions discharge are described.

TABLE 1.4-1

COMPARISON OF MODULE EMISSIONS

Basis: 10^{12}Btu/Day Output Primary Fuels

EMISSIONS AND EFFLUENTS	FUEL OIL[1] REFINERY	GASOLINE[1] REFINERY	PEAK-SHAVING[3] LNG PLANT	BASE LOAD[3] LNG PLANT	SNG PLANT[2]
Air Emissions (lb/day)					
Particulates	6,720	12,300	5,900	2,350	3,750
SO_x	17,000	26,800	790	11,280	1,620
CO	1,280	2,680	5,600	2,540	2,310
NO_x	12,600	35,340	75,800	82,460	41,800
HC	78,700	90,600	47,000	43,200	130,000
Water Effluents (lb/day)					
Suspended Solids	266	295	0	0	0
Dissolved Solids	9,850	10,900	0	0	0
Organic Material	56	62	0	0	negligible
Solid Wastes (lb/day)	8,500	16,500	0	0	0

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[1] Primary fuels for the refinery modules are considered to be the gasoline and middle distillate or light fuel oil product streams. The total heating values of these product streams (gasoline: 5.248x10^6 Btu/bbl, middle distillate: 5.7x10^6Btu/bbl, light fuel oil: 5.825x10^6Btu/bbl) are combined and adjusted to a 10^{12} Btu/day output basis.

[2] Pipeline quality (1000 Btu/SCF) synthesis gas is considered to be the primary fuel from the SNG plant.

[3] Primary fuel from the LNG facility is regasified liquefied natural gas (1000 Btu/SCF).

Refinery, SNG, and LNG plant siting problems are reviewed in Section 6.0. The consequences of emissions to ambient air, wastewater effluents to receiving waters, and solid waste effluents from the plants are discussed. Development of sampling and analytical strategies for hazardous emissions are indicated. Criteria such as raw material supply, energy supply, product transportation, and Federal, state and local laws are also considered.

On the basis of information covered in the preceding sections, suggested priority work for research and development activities are presented in Section 7.0. Among the priority areas considered are studies of air monitoring methods for determining fugitive emissions, and for tracing pollutants in the atmosphere to their sources. Water monitoring and effluent controls and examination of the compositions of solid wastes are also suggested. Cost analyses of future plant design alternatives are discussed.

2.0 PROCESS TECHNOLOGY DESCRIPTION

Descriptions of the present technological positions of petroleum refineries, SNG plants, and LNG plants are presented in this section of the report. The processes and operations associated with each of the three industries are identified and the major processing alternatives discussed. Typical processing sequences are characterized and presented for each industry. The specific purpose of this state-of-the-art review is to provide a basis for the selection of specific modules to represent the technologies for emission determinations.

Also included in this section is a comparison between the operations involved with the refining, SNG, and LNG industries and the processes associated with the new energy technologies of coal gasification, coal liquefaction, and shale oil production. Areas of similarity between the technologies of this report and the new energy systems are identified in order to establish the areas of the new energy technologies to which the emission and control information discussed in this report might apply.

2.1 Petroleum Refining

Petroleum refining is an established industry and, as a result, the technology associated with crude oil refining is well defined. In general, the processing steps involved with refining depend upon the quality of the crude oil and the product distribution required.

Crude petroleum is a mixture of many different hydrocarbon compounds. These compounds are distinguished by their hydrocarbon type and by their normal boiling temperatures. The hydrocarbon types include paraffins, naphthenes, and aromatics, and the normal boiling temperatures encompass a range that exceeds 1000°F for most crudes (NE-044). Effects of crude quality may be minimized to some extent by varying process parameters such as pressure, temperature, and residence time. In addition, refineries receiving a variety of crudes will normally try to mix these crudes in order to achieve a consistent, medium range, feedstock and thus avoid major changes in feed quality as well as extreme crude types.

The factor that impacts processing sequence the most is the product slate required from the refinery. Petroleum refineries are capable of producing a wide range of products and any of these products may be emphasized depending on overall marketing strategy. Major product streams include light hydrocarbons, gasoline, diesel and jet fuels, a light (distillate) fuel oil, and a heavy (residual) fuel oil. Considerable fuel gas is also produced; however, this stream is normally consumed on-site to satisfy process heat requirements. In addition, a portion of the fuel oil make is usually allocated for internal consumption. Other products which may be associated with a refinery include petrochemicals, middle distillates, lube oils, waxes, asphalts, greases, coke, and miscellaneous specialty products.

In general, crude oil is refined by initially separating the crude into various hydrocarbon fractions of specific distillation ranges. Although this separation step is common to all refineries, the processes utilized on the straight run crude fractions following the separation step depend upon the specific refinery requirements.

Possible processing objectives may include:

- treating the straight run streams to remove impurities and undesirable components with the minimum amount of upgrading
- significantly altering the straight run product slate and quality with conversion processes
- obtaining special cuts and utilizing specific processes for lube oil or petrochemical production

Many processes and options are available to a refinery for meeting any of these specific goals.

2.1.1 Refinery Processes

Operations associated with refineries may be roughly categorized into areas of separation, treating, conversion, blending, storage, and auxiliary processes. Conversion processes may be further classified into cracking processes and combination and rearrangement (octane upgrading) processes.

Separation

Although many processes may utilize a distillation train or flash system to separate a process effluent into product streams, the major areas of separation associated with a refinery are crude separation and light end separation.

Crude separation is the initial processing step in refinery operations. The process involves the physical separation of hydrocarbon components in the crude into fractions or intermediates of specified boiling temperature ranges. This operation is well established as the initial processing procedure in a refinery. The main difference between refineries is the type and relative amounts of product streams obtained in the separation process. The degree of separation that is made and the amount of equipment that is required is largely governed by the crude petroleum characteristics (VA-064) and by the products required from the refinery (WH-019). The crude separation may be accomplished in one to three fractionation stages. These stages include one atmospheric plus one or two vacuum fractionation stages.

A topping unit separates the crude in an atmospheric stage only. Streams from a topping unit normally include fuel gas, naphtha, middle distillates, distillate fuel oil, and the reduced crude (atmospheric tower bottoms). Depending upon the refinery objectives the naphtha stream may be split into light and heavy naphtha and the fuel oil into light, middle, and heavy distillate. The differences between the topping unit and other separation processes is that the atmospheric tower bottoms are not separated. This reduced crude stream is normally either used as a heavy fuel oil or routed off-site for further processing.

Crude distillation units employed for separation of the entire crude stream utilize one or two vacuum towers for the heavier fractions. Besides obtaining the same product streams as a topping unit these separation units may either recover additional gas oil from the reduced crude while producing a heavy vacuum resid or else separate the reduced crude into special lube oil cuts along with a resid stream. Normally one vacuum stage is sufficient if the objective is to receive additional gas oil from the reduced crude, whereas, two stages may be utilized if many lube oil cuts are desired. Typical products from a crude distillation unit are shown in Table 2.1-1.

Light ends recovery (sometimes known as vapor recovery) involves the separation of refinery gases from the crude distillation unit and other processing units into individual component streams. The separation is accomplished by absorption and/or distillation. The recovery process that is utilized primarily depends upon the desired purity of the products. For example, an ethane-methane split of refinery gas would require the use of cryogenic fractionation. On the other hand, a reasonable ethane-propane split (60 to 75% propane-propene recovery) can be achieved in conventional fractionation equipment (NE-044).

Treating

Streams from the crude separation step contain sulfur compounds and other undesirable components which must be removed due to the effect on product quality, catalyst sensitivity, odor, and corrosivity. Although refiners originially could treat only select streams, all streams from the crude distillation unit can now be desulfurized except for residua. Desulfurization processes utilized in a refinery include both gas treating and hydrotreating processes.

TABLE 2.1-1

TYPICAL PRODUCTS FOR CRUDE DISTILLATION

Crude Fraction	Typical Boiling Range
Light Ends	C_4 and lighter
Light Naphtha	30 - 300°F
Heavy Naphtha	300 - 400°F
Kerosine	400 - 500°F
Light Gas Oil	400 - 600°F
Heavy Gas Oil	600 - 800°F
Vacuum Gas Oils	800 - 1100°F
Residue	>1100°F

Source: (BL-078)

Refinery gases separated in the crude distillation unit and produced in various processing units contain a variety of acid gas species, of which the major contaminant is hydrogen sulfide. These acid gases are normally removed from the light ends in a gas treating unit by absorption with an aqueous regenerative solvent. A number of gas treating processes are available and they are distinguished primarily by the regenerative sorbent employer. Examples of gas treating processes which may be utilized are presented in Table 2.1-2. Amine-based sorbents are most commonly used in refinery applications (NG-002).

Desulfurization of petroleum cuts by hydrotreating is widely practiced in modern refineries because of: (1) environmental protection laws limiting the sulfur levels in fuels; (2) the decrease of available low sulfur crudes; (3) the undesirable properties of sulfur and sulfur compounds including corrosiveness, odor, color, instability, and catalyst poisoning tendencies; and (4) hydrotreating petroleum stocks catalytically converts organic compounds of sulfur, nitrogen, and oxygen into hydrocarbons and removable sulfide, ammonia, and water. Although a stream encompassing several product cuts may be desulfurized at one time (as in crude desulfurization), petroleum fractions are normally hydrotreated separately due to the varying sulfur limits on the various fuels and the wide range of catalysts and reactor conditions required to hydrotreat the various petroleum fractions. Hydrotreaters for naphtha, middle distillate, distillate fuel oil, and residual oil streams are utilized in refineries. Desulfurization is also achieved in a hydrocracker, but the main purpose of this process is to crack a straight run gas oil cut or a cycle gas oil from a FCCU to gasoline and jet fuel fractions. Likewise slight desulfurization of residual or lube oil fractions is accomplished in a hy-finishing process in which the lube oil cut is mildly hydrogenated over a fixed bed catalyst. Although some desulfurization results, objective of this process might be color improvement or oxidation stability.

TABLE 2.1-2
GAS TREATING PROCESSES

Name	Solvent	Licensor
	AMINE SYSTEMS	
Adip	Alkanolamine	Shell
Fluor Econamine	DGA	Fluor
SNPA	DEA	Parsons
Sulfinol	Tetrahydrothiolene Dioxide & Alkanolamine	Shell
	ALKALI-CARBONATE SYSTEMS	
Benfield	Potassium carbonate solution with Benfield additives	Benfield
Catacarb	Potassium salt solution with additives	Eickmeyer
Giammarco Vetrocoke	Potassium carbonate with arsenic trioxide	Vetrocoke
	PHYSICAL ABSORPTION SYSTEMS	
Fluor Solvent	Propylene Carbonate	Fluor
Purisol	N-Methyl-Pyrrolidone	Lurgi
Rectisol	Methanol	Lurgi
Selexol	Dimethyl Ether of Polyethylene Glycol	Allied

Cracking

Cracking processes convert heavy oils into petroleum fractions of lower boiling range and correspondingly lower molecular weight. These processes are very important in respect to the quantity of gasoline or other light products obtained from a barrel of crude. General categories of cracking processes are thermal cracking, fluid catalytic cracking, and hydrocracking.

The thermal cracking concept was the first cracking process to be developed and employed in refineries due to the simplistic approach involved with just heating the hydrocarbon fractions. Different thermal cracking processes and applications are as follows:

(1) Thermal cracking of gas oil for naphtha or gasoline production - the original service of the thermal cracking process, this application has mostly been taken over by more sophisticated processes such as fluid catalytic crackers or hydrocrackers. The disadvantage of thermal cracking is that the process is not selective and consequently the yield of desired product is relatively low. An advantage of this operation is that the simplicity of the process combined with the fact that no catalyst is employed allows a thermal cracker to handle almost any process stream.

(2) Visbreaking - visbreaking is a mild variation of thermal cracking applied to a residual fuel oil or reduced crude. The mild conditions (880°F) are to minimize coke formation.

The specific purpose of visbreaking is to reduce the viscosity of the feed so as to lessen the amount of blending stock required to upgrade the feed to fuel oil specifications.

(3) Delayed coking - delayed coking is applied to a residual stream and uses severe conditions (1800°F-2000°F) to crack the feedstock to a coke gas, distillates, and coke.

(4) Fluid coking - fluid coking is a newer and more flexible coking process. Fluid coking converts the residual stream to higher value products and results in less coke than delayed coking (HA-282).

The primary advantages of catalytic cracking over thermal cracking are in the production of a maximum of light hydrocarbons at C_4 rather than at C_2 and a higher yield of light gasoline compounds (C_5 and C_6). Gasoline from a catalytic cracker is also higher in branched paraffins, cycloparaffins, and aromatics, all of which increase the quality of the gasoline.

Feedstocks to catalytic cracking include gas oils from both atmospheric and vacuum distillation and cracked fractions from such processes as delayed or fluid coking.

Hydrocracking is a very flexible process which cracks the feed in the presence of a high hydrogen partial pressure (1200-1700 psi). Hydrocracking may be applied to any stream; however, a gas oil stream is the usual feed. Hydrocracking is normally used on a high sulfur straight run gas oil that would be unsatisfactory for catalytic cracking or on a gas oil effluent from another cracking process. Hydrocracking complements catalytic cracking and provides flexibility in meeting various product demands. Products from a hydrocracker may include light ends, light gasoline, heavy gasoline, and middle distillate. Heavier fractions are normally recycled to extinction. Hydrocrackates are saturated and are higher in branched chains than catalytic cracking processes.

Combination

Combination processes normally combine two light hydrocarbons to produce a gasoline range hydrocarbon. Either a polymerization process or an alkylation process may be used for this purpose. A polymerization process combines two or more gaseous olefins into a liquid product. An alkylation process joins an olefin and an isoparaffin (isobutane) in order to produce a gasoline range hydrocarbon. The olefin feed to either unit is usually obtained from the catalytic cracker. Isoparaffins for an alkylation unit may be supplied from a hydrocracker. Both processes utilize catalyst such as phosphoric, sulfuric, or hydrofluoric acid.

Alkylation has grown at the expense of polymerization due to two distinct advantages. A polymerization unit yields 1.0 bbl of gasoline for every 1.4 bbl olefin feed, whereas, 1.4 bbl of olefin combined with isobutane is an alkylation process yields approximately 2.5 bbl of alkylate (HY-008). In addition, the alkylate has a motor octane rating approximately 12 octane numbers higher than the polymer product. As a result, alkylation processes are primarily utilized to obtain gasoline components from olefin. Polymerization processes in this service are mainly older units. Polymerization of olefins is employed for the production of petrochemicals.

Rearrangement

The primary purpose of rearrangement processes is to change (rearrange) the molecular structure of the feedstock to produce a high quality stream for gasoline blending. The two major rearrangement processes in the refinery are catalytic reforming and isomerization.

Catalytic reformers convert low octane naphthas into high octane naphthas by catalytically rearranging and dehydrogenating naphthenes and paraffins, forming aromatics such as benzene, toluene, and xylenes. Reformer feedstock is normally a desulfurized straight run or cracked naphtha (100-400°F). The high octane aromatic products may be used for gasoline blending or used for petrochemical feedstocks. Heavy naphthas are usually fed when making gasoline and light naphthas when making aromatics for the petrochemical industry (NA-182). If the refinery is emphasizing petrochemicals, a liquid-liquid aromatic extraction unit may be incorporated within the catalytic reformer. The aromatic extraction unit separates the reformate stream into a raffinate stream containing the non-aromatics and an extract stream containing 95% aromatics (DE-070). Hydrogen is also produced (800-1500 scf/bbl of feed) as a part of the reforming process (NA-182). This aspect of catalytic reformers is important in supplying the total hydrogen demand of the refinery. Hydrogen from the reformer does not require desulfurization since the reformer feed streams are previously hydrotreated to protect the reformer catalyst. Total streams from the reformer usually include the reformate, light ends, and hydrogen.

Isomerization units are used to increase the octane rating of pentane and hexane fractions by rearranging the normal paraffins into isoparaffins. The feed to an isomerization unit is normally desulfurized straight chain pentane and hexane fractions. The product is a low sensitivity gasoline blending stock consisting of up to 75% isomers and having a clear research octane number of 80 to 85 (RI-044). The reaction takes place over a chlorinated platinum-aluminum-oxide catalyst at a temperature of 320°F and a pressure of 400 psig (LA-078). This process may also produce isobutanes for alkylation if this compound is not sufficiently generated by the other refinery processes. Any IC_4 produced is routed to alkylation while the C_5/C_6 effluent goes to gasoline blending.

Blending

Refinery blending operations involve the mixing of various components to achieve a product of desired characteristics. Blending operations are associated with the final products of gasoline, aviation fuels, heating fuels, lubricating oils, greases, and waxes. The relatively few base and intermediate stocks may be blended to produce over 2000 finished products (NA-182). Although small volume blending may be performed in a mixing vessel, bulk product blending is normally achieved as an in-line operation prior to product tankage.

The most common blending operation in petroleum refineries involves the final step in the preparation of gasoline. Various gasoline components such as catalytically cracked gasoline, hydrocrackate, reformate, isomerate, alkylate, and butane are combined with additives such as dye and tetraethyl lead (TEL) in the necessary proportion to meet gasoline marketing specifications. This blending is normally accomplished in a mixing manifold prior to storage.

Storage

Storage capacity is required for liquid feedstocks, intermediate products, and final products. There are five basic types of storage tanks used by refineries. These include fixed roof, floating roof, internal floating cover, variable space, and pressure. The application of these tanks largely depends on the volatility of the stored liquid.

The fixed roof tank is the least expensive and the most common type of tank used. It is a cylindrical steel tank with a conical steel roof. Today fixed roof tanks are normally equipped with pressure/vacuum valves set at only a few inches of H_2O to contain minor vapor volume expansion.

Floating roof tanks are cylindrical steel tanks similar to fixed roof tanks. However, instead of a fixed roof, they are equipped with a sliding roof, designed to float on the surface of the product. A sliding seal attached to the roof seals the annular space between the roof and vessel wall from product evaporation. Floating roof tanks eliminate the vapor space of fixed roof tanks.

Internal floating covers are a modification of floating roofs, designed to deal with the buoyancy problems caused by snow and rain. They are essentially fixed roof tanks equipped with an internal floating cover similar to a floating roof. Internal floating covers contain sliding seals to seal the annular space between the cover and the vessel wall from evaporation.

There are two basic types of variable vapor space tanks, lifter roof and diaphragm. The lifter roof tank has a telescopic roof, free to travel up and down as the vapor space expands and contracts. A second type is the diaphragm tank equipped with an internal flexible diaphragm to cope with vapor volume changes.

Pressure tanks are used to store highly volatile products. These tanks come in a very wide range of shapes and are designed to eliminate evaporation emissions by storing the product under high pressures. Pressure tanks are commonly designed for pressures up to 200 psig.

Fixed roof, floating roof, and internal floating cover tanks are the most common tanks in refinery service. These tanks range in size from 20,000 to 500,000 bbl and average 70,000 bbl (MS-001).

Table 2.1-3 indicates the vapor pressures (EN-043), volumes (MS-001), and types of storage tanks used for several major refinery products. Federal emission regulations currently require hydrocarbon products with true vapor pressures (under storage temperatures) ranging from 1.5 to 11.1 psia be stored in floating roof tanks or their equivalent. Normally internal floating covers are considered equivalent to floating roof tanks.

TABLE 2.1-3

NATURE OF PRODUCT STORAGE AT REFINERIES

Product	True Vapor Pressure psia @ 60°F	Types of Storage Tanks	Qty. Stored 1968 (10^6bbl)
Fuel Gas	--	Cryogenic - Pressurized	
Propane	105	Pressurized	
Butane	26	Pressurized	
Motor Gasoline	4-6	Vapor Saver, Fixed Roof, Floating Roof	204
Aviation Gasoline	2.5-3	Vapor Saver, Fixed Roof, Floating Roof	14
Jet Naphtha	1.1	Vapor Saver, Fixed Roof, Floating Roof	18
Jet Kerosene	<0.1	Fixed Roof	31
Kerosene	<0.1	Fixed Roof	46
No. 2 Distillate	<0.1	Fixed Roof	346
No. 6 Residual	<0.1	Fixed Roof	
Crude Oil	2	Vapor Saver, Fixed Roof, Floating Roof	137

Auxiliary Operations

A number of important auxiliary operations are required in petroleum refining. These auxiliary operations include such processes as crude desalting, hydrogen production, sulfur recovery, water treatment, and power generation.

Crude Desalting

Crude desalting is normally the first unit in an oil refinery. The function of this unit is to remove the inorganic salts and brines from the incoming crude in order to prevent process fouling, corrosion, and catalyst poisoning. Crude may be desalted by either electrical or chemical means. Electrostatic crude desalting is the more prevalent process (RA-119). In this process incoming crude is heated and then mixed with water and passed through an emulsifier. The water-oil emulsion is then routed through a treating vessel where a high voltage field demulsifies the oil and water. Impurities from the crude oil are removed in the water effluent.

Chemical crude desalting utilizes coalescing agents instead of a high voltage field to demulsify the aqueous and organic phases.

Hydrogen Generation

Hydrogen is consumed in many refinery processes including hydrotreating, hydrocracking, and isomerization. Hydrogen must be available in order for these units to operate efficiently; therefore, a plant hydrogen balance must be maintained. Although a large portion of the hydrogen demand of a refinery may be supplied by catalytic reformers, these units cannot normally supply a sufficient amount of hydrogen to meet the total refinery demand. A hydrogen generation unit is utilized to provide the balance of the refinery hydrogen demand.

Hydrogen may be produced by either steam-hydrocarbon reforming or partial oxidation. In steam hydrocarbon reforming the steam is catalytically reacted with a light hydrocarbon such as methane or naphtha to produce hydrogen. Reaction temperature is approximately 1700°F (HY-007). The generalized reforming reaction is

$$C_nH_m + nH_2O \rightleftarrows nCO + \frac{(2n+m)}{2} H_2 .$$

In partial oxidation a hydrocarbon feedstock is partially combusted with oxygen and steam, producing hydrogen from the following reactions.

$$C_nH_m + \frac{n}{2} O_2 \rightleftarrows nCO + \frac{m}{2} H_2$$

$$C_nH_m + nH_2O \rightleftarrows nCO + \frac{(2n+m)}{2} H_2$$

The water gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

establishes the final gas composition in both processes and then the CO_2 is removed. Options in hydrogen production result from the fact that steam-hydrocarbon reforming was developed for a gas or naphtha feed, while partial oxidation accommodates a heavy residual oil feed.

Sulfur Recovery

Sulfur recovery involves conversion of the hydrogen sulfide content of acid gases into elemental sulfur. The Claus process is the widely accepted process for sulfur recovery in the refinery industry. The H_2S is combusted with a sub-stoichiometric air supply producing sulfur, sulfur dioxide and water.

$$H_2S + \tfrac{1}{2}O_2 \rightleftarrows S + H_2O$$

$$H_2S + 3/2\ O_2 \rightleftarrows SO_2 + H_2O$$

Additional sulfur recovery is obtained in a series of catalytic reactors by reacting H_2S with SO_2. The number of reactors utilized in the Claus unit is the main refinery option since conversion varies with the number of reactors employed. Potential sulfur recovery efficiencies for the different number of conversion stages and % H_2S in the feed are shown in Table 2.1-4.

Tail gas from the Claus plant can be further treated by a tail gas treating unit. Many tail gas treating processes are available, utilizing many different reaction mechanisms. Examples of tail gas processes are given in Table 2.1-5. Utilizing a tail gas treating unit in conjunction with a Claus plant usually increases the total sulfur recovery to between 99-99.9% depending upon the Claus plant efficiency and the specific tail gas process employed.

Water Treating

Many options are available to the refiner concerning wastewater handling. These alternatives include options in

- refinery equipment,
- in-plant pretreatment versus a waste treatment plant,
- segregation of wastewater streams, and
- degree of primary, secondary, and tertiary treatment.

TABLE 2.1-4

TYPICAL CLAUS PLANT SULFUR RECOVERY FOR VARIOUS FEED COMPOSITIONS WITH AVERAGE ORGANIC BY-PRODUCTS AND ENTRAINMENT ALLOWANCE

Hydrogen sulfide in sulfur plant feed (dry basis) %	Calculated percentage recovery		
	Two reactors	Three reactors	Four reactors
20	92.7	93.8	95.0
30	93.1	94.4	95.7
40	93.5	94.8	96.1
50	93.9	95.3	96.5
60	94.4	95.7	96.7
70	94.7	96.1	96.8
80	95.0	96.4	97.0
90	95.3	96.6	97.1

Source: (BA-166)

TABLE 2.1-5

PROCESSES USED FOR SULFUR REMOVAL FROM CLAUS TAIL GAS

SOURCE: (BA-166)

Name	Developer	Ref.	Operation	Abstract	Extraneous process feed streams required	Sulfur removal	Product
Beavon Sulfur Removal Process	Ralph M. Parsons & Union Oil Co. of California	13, 16	Los Angeles refinery, Union Oil Co. of California	Tail gas from Claus sulfur recovery plant is catalytically hydrotreated at atmospheric pressure. All sulfur compounds are converted to H_2S which is then processed through a Stretford unit.	Fuel gas and air	Removal to 250 ppm SO_2 or less	Sulfur
CleanAir Sulfur Process	J. F. Pritchard & Co. and Texas Gulf Sulfur Co.	17, 18	Pilot plant work, Okotoks plant, Texas Gulf Sulfur Co. Philadelphia refinery, Gulf Oil Co.	Three stage process: Stage 1 converts essentially all SO_2 to sulfur with some conversion of H_2S to sulfur. Stage 2 converts remaining hydrogen sulfide to sulfur in a Stretford unit. Stage 3 is a polishing unit to reduce the COS and CS_2 level in the tail gas which is normally installed between the Claus plant and Stage 1.	Fuel gas and air	Removal to 250 ppm SO_2 or less	Sulfur
IFP Sulfur Recovery Process	Institut Francais du Petrole	20, 21	Demonstration plant, Lone Pine Creek plant, Hudson's Bay Oil & Gas Co. Nippon Petroleum Refining Co., Japan Idemitsu Oil Co., Japan Kyokutoh Oil Co., Japan Showa Oil Co., Japan	Tail gas from a Claus unit is fed into an absorber, where the Claus reaction occurs in a solvent in the presence of a catalyst. Sulfur is produced in the molten state directly from the base of the absorber. No conversion of COS and CS_2 is claimed.	None	SO_2 removal to 1,000 ppm	Sulfur
Shell's Flue Gas Desulfurization Process	Koninklijke/Shell Laboratorium, the Netherlands	14	Pilot plant work, Pernis, the Netherlands Yokkaichi refinery of Showa-Hokkaichi Oil Co.	Dry process for removing SO_2 from flue gas from the incinerator in a parallel passage solid bed swing reactor. This is a cyclic process in which a copper on alumina acceptor is used for acceptance and regeneration of the SO_2 at 750° F. A purge gas stream to separate the oxidizing and reducing atmospheres is required for both the acceptance and regeneration steps. SO_2 concentration step is required.	Reducing gas H_2, H_2/CO mixtures, or light paraffinic hydrocarbons	90% SO_2 removal	SO_2 formed is recycled through a Claus unit
SNPA-Sulfuric Acid Process	SNPA and Haldor Topsoe	5, 15	SNPA sulfur plant, Lacq field	Tail gas is incinerated transforming all sulfur compounds to SO_2. The gas is then passed through a converter containing a vanadium oxide-based catalyst. SO_2 is oxidized to SO_3 with a 90% yield. The hot converter gas exchanges heat in the concentrator, and then goes through an absorber. Dilute acid produced is then sent to a concentrator in which the heat content of gas from the convertor evaporates part of the water from the acid.	Fuel gas and air	90% SO_2 conversion	94% sulfuric acid
Sulfreen Process	SNPA and Lurgi Gesellschaften	5, 15, 19	SNPA sulfur plant, Lacq field Aquitaine's Ram River sulfur plant, Rocky Mountain House, Alberta	Activated carbon bed catalyzes the Claus reaction between the H_2S and SO_2 in tail gas and adsorbs elemental sulfur formed. Inert regeneration gas is used at elevated temperatures to desorb the sulfur. Bed is then cooled and placed back on reaction cycle. No conversion of COS and CS_2 is claimed.	Inert gas for regeneration	75% of sulfur in the Claus plant tail gas	Sulfur
Wellman-SO_2 Recovery Process	Wellman Power Gas	11, 12, 13, 24	Olin Chemical Co., Paulsboro, N. J. Japanese Synthetic Rubber Co., Chiba, Japan Toa Nenryo Kogyo refinery, Kanagawa, Japan Standard Oil refinery, El Segundo, Calif. Allied Chemical Co. sulfuric acid plant, Chicago Olin Corp. sulfuric acid plant, Curtis Bay, Md.	Sulfur plant incinerator effluent is cooled to 150° F and contacted with a sodium sulfite solution. SO_2 in the gas reacts to form sodium bisulfite. The gas can be stripped to low concentrations of SO_2. Alternative regeneration schemes have been used. In one plan, the SO_2 rich solution from the absorber flows into an evaporator/crystallizer where the bisulfite decomposes to SO_2 and the sodium sulfite crystals precipitate. Sulfite crystals are redissolved to be recirculated. The regenerator overhead is cooled and SO_2 and water vapor recycled to Claus plant. Sodium hydroxide chemical makeup is required.	None	SO_2 removal to 100 ppm	60% SO_2 and 40% water vapor

Options in design will effect the amount of wastewater generated. Alternative processes and equipment which can significantly reduce the wastewater load in a refinery are shown in Table 5.2-1.

In-plant pretreatment processes are considered the water treating facilities located upstream of the process wastewater treating plant. The amount of in-plant pretreatment utilized is a major alternative since this pretreatment may often be more efficient and economical than the waste treatment plant. In-plant pretreatment processes include sour water strippers, spent caustic oxidizers, spent caustic neutralizers, and chlorination of sanitary wastes.

Another area of difference in wastewater handling is in the segregation of water streams. Good effluent segregation systems can significantly reduce the cost of wastewater handling and treatment. Effluent may be separated according to dissolved solids content, oil content, phenol content, sulfide content, toxic chemical content and sanitary sewage content.

Waste treatment plants differ in the amount of primary, secondary and tertiary treatment utilized. Primary treatment facilities are involved in the physical upgrading of aqueous effluents prior to discharge or secondary treatment. Primary treatment processes include API separators; settling chambers and clarifiers; air flotation, coagulation, and flocculation systems; and alkaline and acidic neutralization. Secondary treatment is for the removal of BOD and COD from wastewater. Secondary treatment methods include aerobic biological treatment, anerobic biological treatment, and chemical oxidation using chlorine or ozone. The most common secondary method is aerobic biological treatment in aerated lagoons. Tertiary treatment consists of more severe water processing. Tertiary treatment may be considered to consist of processes such as activated carbon treatment, ion exchange, reverse osmosis, and evaporation. Although these processes are not now commonly employed, as refineries move toward zero wastewater discharge tertiary treatment will be used more extensively.

Power Generation

Although all refineries require steam generation, the specific refining processes employed and the overall plant steam balance determine whether a steam generation facility in continuous operation is necessary. Refineries producing a large amount of steam from processes such as the FCCU CO boiler may only require a steam boiler as a backup system, whereas other refineries require steam generation facilities in continuous operation. Likewise many refineries rely on an outside supply of electricity while others, utilize a power plant for electrical generation. Major factors effecting the utilization of electrical generation facility are the availability and cost of outside electricity and the refinery electrical demands.

Petroleum Refinery Categories

Although no two refineries are exactly alike, petroleum refineries may be classified in general groups according to either (1) the general purpose of the refinery (portion of the product slate emphasized) or (2) any specialty processing associated with the refinery such as lube oil or petrochemical processing. Topping, fuel oil, and gasoline refineries each produce a different product yield structure and consequently utilize significantly different processing sequences. Refineries producing lube oils or petrochemicals employ special processes on selected process streams; however, the greater part of the refinery may be essentially a fuel oil or gasoline processing sequence. For this review, petroleum refineries are classified into the following five basic categories:

(1) topping refineries,

(2) fuel oil refineries,

(3) gasoline refineries,

(4) lube oil refineries, and

(5) petrochemical refineries.

Topping Refinery

The topping refinery is the simplest of the basic refinery types. The topping or skimming operation is a simple atmospheric-pressure distillation. The purpose of this type of refinery is to obtain the atmospheric straight run fractions such as naphtha, middle distillate, and fuel oil from the crude stream.

A topping refinery does not typically utilize many upgrading operations. Middle distillate and fuel oil streams are normally desulfurized and routed to product tankage. The straight run naphtha stream is desulfurized and may be either marketed as such or upgraded further with a catalytic reformer. If the naphtha stream is not upgraded with a catalytic reformer, a hydrogen generation unit such as a steam-naphtha reformer is required in order to supply hydrogen to the hydrotreaters. Other processing units which may be associated with a topping refinery include a gas treating unit for light ends and a sulfur recovery unit. The reduced crude from the topping unit (atmospheric tower bottoms) is routed off-site for further processing.

A processing sequence for a topping refinery is shown in Figure 2.1-1. The crude oil is initially split into the straight run fractions of light ends, naphtha, heavy naphtha, distillate fuel oil, and reduced crude oil. The light ends are normally treated for acid gas removal and either used for fuel gas or separated for petrochemical feedstocks. Light naphtha is stabilized, hydrotreated and routed to gasoline blending. Straight run heavy naphtha is hydrotreated and catalytically reformed prior to routing to gasoline blending. Distillates are hydrotreated and routed to product storage as distillate fuel oil. Reduced crude oil is either routed to tankage as a heavy fuel oil or goes off-site for further processing.

The processing sequence utilized in a topping refinery is essentially duplicated in the other major categories of refineries since atmospheric distillation is normally the first major operation in all refineries and all straight run streams are usually sweetened in refineries prior to further processing. Since conversion processes are not normally associated with topping refineries, the product yield and distribution is directly related to crude quality.

Fuel Oil Refinery

A fuel oil refinery utilizes a processing sequence established to promote the yield of product fuel oil. The fuel oil produced may be approximately 40-60 vol% of the liquid product with the bulk of the remainder of the products being gasoline.

Major elements in this type of refinery include a crude distillation unit to separate the feed into straight run fractions, light end treating and recovery units, hydrotreaters for the crude distillation cuts, naphtha upgrading processes, and thermal cracking or coking units for the heavy resid.

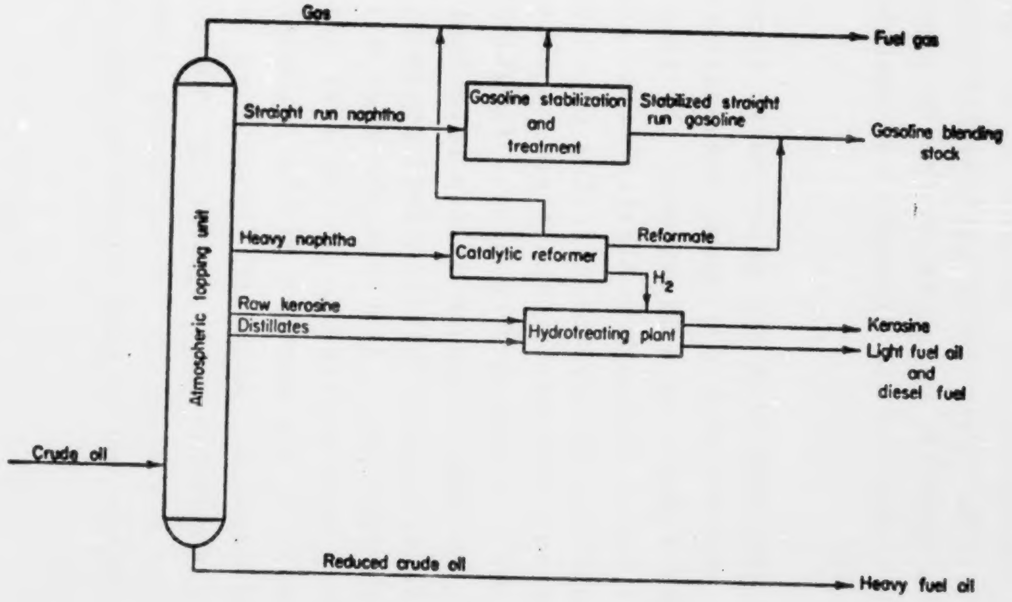

Gas
Fuel gas
Straight run naphtha
Gasoline stabilization and treatment
Stabilized straight run gasoline
Gasoline blending stock
Atmospheric topping unit
Heavy naphtha
Catalytic reformer
Reformate
H_2
Raw kerosine
Distillates
Hydrotreating plant
Kerosine
Light fuel oil and diesel fuel
Crude oil
Reduced crude oil
Heavy fuel oil

FIGURE 2.1-1 PROCESSING PLAN FOR TYPICAL TOPPING REFINERY

Source: EL-065

A flow diagram for a typical fuel oil refinery is shown in Figure 2.1-2.

This type of refinery utilizes essentially the same processes as the topping refinery, but also includes units for processing the heavy crude fractions - crude distillation, propane deasphalting, flexicoker, and deasphalted oil hydrotreater. In addition units for octane improvement such as isomerization and catalytic reforming are normally utilized in the fuel oil refinery. These two units upgrade the straight run naphtha stream to motor gasoline quality.

Fuel oil is obtained from the heavy resid stream by (1) extraction of the asphalt with a propane deasphalting unit and (2) cracking of the asphalt in a flexicoker to yield light ends, naphtha and fuel oil. Although a flexicoker is shown in this processing sequence any of several cracking processes such as delayed coking and visbreaking which are capable of handling the heavy asphalt stream may be used. Flexicoking was chosen as typical, however, because of its potential to produce more of the lighter, more valuable fuel products such as naphtha and refinery fuel gas. Although the fuel oil product is increased by cracking heavier fractions, the fuel oil yield is not normally increased at the expense of the gasoline available from straight run naphtha. Although flexicoking is not currently being used extensively in the refining industry, the process appears to offer a viable way for achieving greater naphtha and fuel oil yields and as such should see greater utilization in the future.

Gasoline Refinery

In a refinery emphasizing gasoline production, extensive cracking and upgrading facilities are utilized in order to produce and refine the gasoline. A flow diagram for a typical

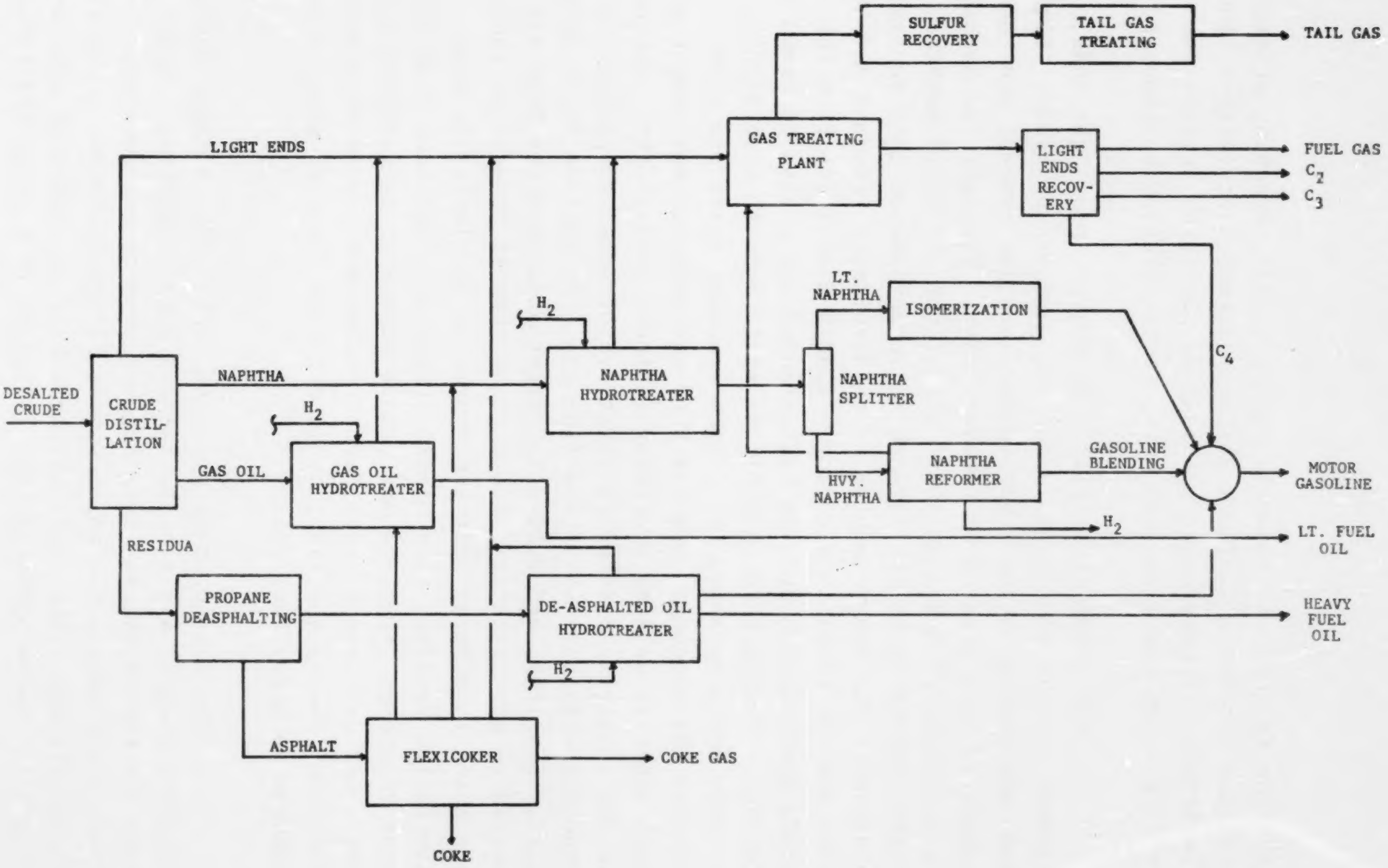

TAIL GAS
SULFUR RECOVERY
TAIL GAS TREATING
LIGHT ENDS
GAS TREATING PLANT
LIGHT ENDS RECOVERY
FUEL GAS
C_2
C_3
LT. NAPHTHA
ISOMERIZATION
C_4
H_2
NAPHTHA
DESALTED CRUDE
CRUDE DISTILLATION
NAPHTHA HYDROTREATER
NAPHTHA SPLITTER
GAS OIL
GAS OIL HYDROTREATER
HVY. NAPHTHA
NAPHTHA REFORMER
GASOLINE BLENDING
MOTOR GASOLINE
LT. FUEL OIL
RESIDUA
PROPANE DEASPHALTING
DE-ASPHALTED OIL HYDROTREATER
HEAVY FUEL OIL
ASPHALT
FLEXICOKER
COKE GAS
COKE

FIGURE 2.1-2 FUEL OIL PROCESSING SEQUENCE

gasoline refinery is shown in Figure 2.1-3. Cracking processes utilized include a fluid catalytic cracker, hydrocracker, and flexicoker. Upgrading or rearranging processes include two reformers, an isomerization unit, and an alkylation process.

Raw crude is initially separated into light ends, naphtha, middle distillates, gas oil, and vacuum resid. Light ends are routed to gas treating for acid gas removal and then separated in a light ends recovery unit. Straight run naphtha is hydrotreated and then split into light and heavy naphtha. The light naphtha is routed through an isomerization unit to gasoline blending. The heavy naphtha is catalytically reformed and then also goes to gasoline blending. Middle distillate from the crude distillation unit is hydrotreated and routed to product tankage. Straight run gas oil is split between a catalytic cracker and a hydrocracker. Both cracking units are used because the products from the FCCU and hydrocracker complement each other as well as providing refinery flexibility. Gas oil to the catalytic cracker is first hydrotreated to protect the cracking catalyst. Products from the FCCU include light ends, C_3/C_4, gasoline, and fuel oil. Light ends from the FCCU are routed to gas treating. The C_3/C_4 stream is treated by caustic scrubbing in a Merox unit and routed to an alkylation unit. The alkylation receives this olefin stream and isobutane from light ends recovery. Alkylate and excess butane go to gasoline blending. Cat gasoline is also Merox treated and routed to gasoline blending. Heavy and light cycle oil from the FCCU goes to product tankage as heavy fuel oil.

The hydrocracker produces light ends, a light naphtha (hydrocrackate), and a heavy naphtha (hydrocrackate). Light ends are routed to gas treating and then to gas recovery. These light ends are a major source of the isobutane required for alkylation. The light hydrocrackate is routed to gasoline blending. Heavy hydrocrackate is routed to a catalytic reformer

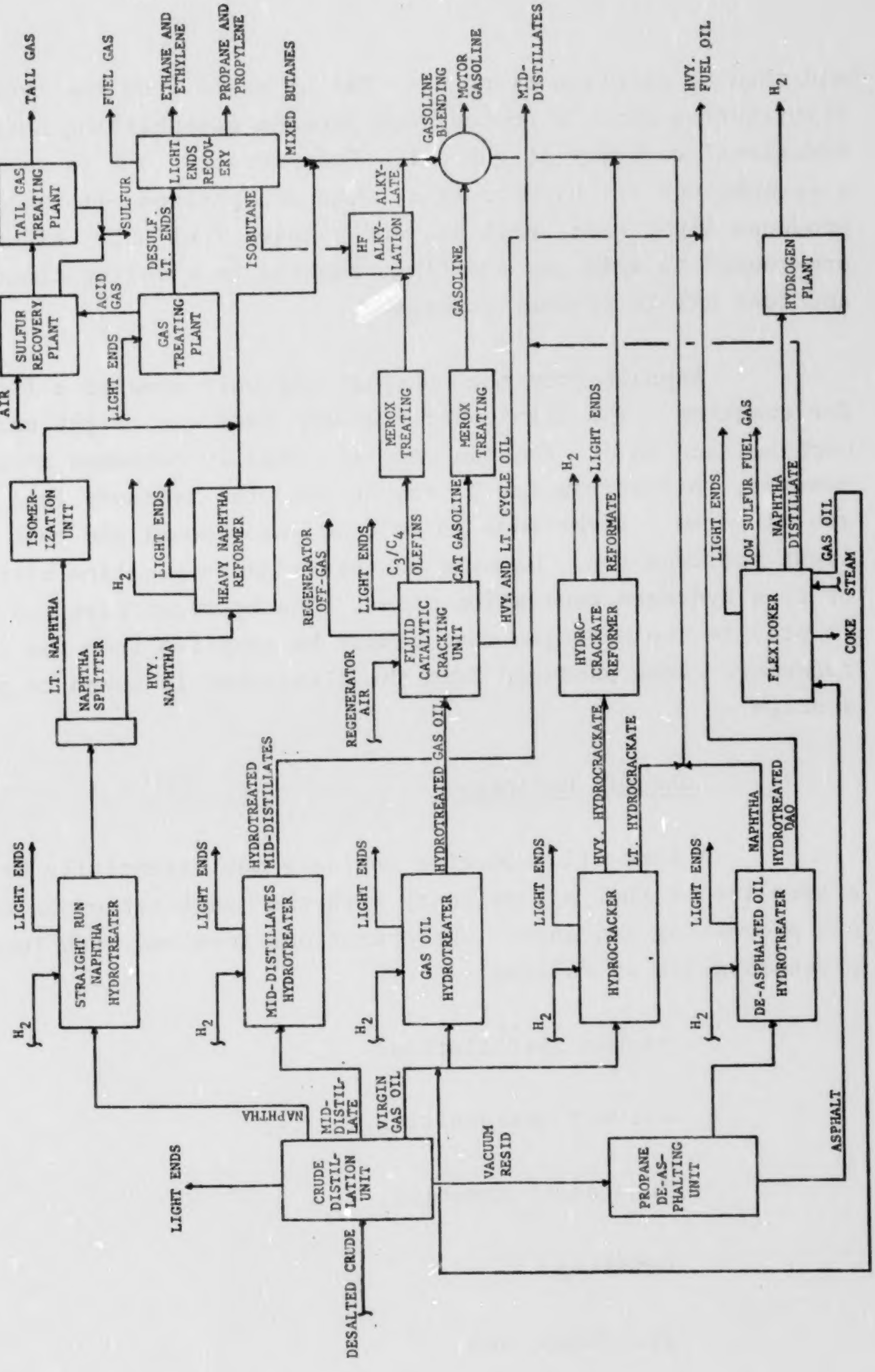

DESALTED CRUDE
CRUDE DISTIL-LATION UNIT
LIGHT ENDS
NAPHTHA
MID-DISTIL-LATE
VIRGIN GAS OIL
VACUUM RESID
PROPANE DE-AS-PHALTING UNIT
ASPHALT
H_2
STRAIGHT RUN NAPHTHA HYDROTREATER
LIGHT ENDS
MID-DISTILLATES HYDROTREATER
HYDROTREATED MID-DISTILIATES
GAS OIL HYDROTREATER
HYDROTREATED GAS OIL
HYDROCRACKER
HVY. HYDROCRACKATE
LT. HYDROCRACKATE
DE-ASPHALTED OIL HYDROTREATER
NAPHTHA
HYDROTREATED DAO
NAPHTHA SPLITTER
LT. NAPHTHA
HVY. NAPHTHA
ISOMER-IZATION UNIT
HEAVY NAPHTHA REFORMER
REGENERATOR AIR
REGENERATOR OFF-GAS
FLUID CATALYTIC CRACKING UNIT
C_3/C_4 OLEFINS
CAT GASOLINE
HVY. AND LT. CYCLE OIL
HYDRCRACKATE REFORMER
REFORMATE
FLEXICOKER
COKE
STEAM
GAS OIL
NAPHTHA DISTILLATE
LOW SULFUR FUEL GAS
AIR
SULFUR RECOVERY PLANT
GAS TREATING PLANT
ACID GAS
TAIL GAS TREATING PLANT
TAIL GAS
SULFUR
DESULF. LT. ENDS
LIGHT ENDS RECOVERY
FUEL GAS
ETHANE AND ETHYLENE
PROPANE AND PROPYLENE
MIXED BUTANES
ISOBUTANE
MEROX TREATING
MEROX TREATING
GASOLINE
HF ALKY-LATION
ALKY-LATE
GASOLINE BLENDING
MOTOR GASOLINE
MID-DISTILLATES
HVY. FUEL OIL
HYDROGEN PLANT

FIGURE 2.1-3 GASOLINE REFINERY PROCESSING SEQUENCE

and then to gasoline blending. Vacuum resid from the crude distillation unit is routed to a propane deasphalting unit for additional recovery of gas oil. The extracted oil is routed to a deasphalted oil hydrotreater. The deasphalted oil hydrotreater produces light ends, naphtha, and a heavy fuel oil. Light ends are routed to acid gas treating, naphtha to gasoline blending, and fuel oil to product tankage.

Asphalt from the deasphalting unit goes to a flexicoker for cracking. The flexicoker produces fuel gas, light ends, naphtha, and coke. The fuel gas is normally consumed at the unit; however, this stream can be routed into the refinery fuel gas mix drum. Light ends go to acid gas removal and then to light end recovery. Naphtha may be routed to gasoline blending or to a hydrogen generation plant. The hydrogen plant is required to provide the hydrogen that cannot be supplied from the catalytic reformer. Coke produced from the flexicoker is taken to product storage.

Lube Oil Refinery

A lube oil producing refinery may essentially be either a gasoline or fuel oil refinery with the modification of the lube oil processing sequence. The operations involved with lube oil processing are as follows:

- vacuum distillation,
- solvent deasphalting,
- lube stock treating,
- dewaxing,
- finishing, and
- blending and compounding.

Individual raw lube oil fractions are cut at the vacuum distillation tower of the crude distillation unit. Preferred lube oil stocks are high-boiling paraffins with several side chains. Normally three to five lube stocks are separated on the vacuum tower.

Heavy oil from the vacuum tower is routed to a solvent deasphalting unit. Propane is normally the solvent utilized. Asphaltenes entrained in the lube oil streams must be removed since they have an adverse effect in processing in other lube oil units - poor color and lower yield from treating, slower filtration in solvent dewaxing, and more coking in hy-finishing. The deasphalting unit produces an asphalt and a heavy lube oil known as "brightstock."

Deasphalted oil is routed to treating processes to improve the viscosity characteristics, color, and carbon residue content. Treating processes which may be utilized include sulfuric acid treating, phenol extraction and furfural treating. In sulfuric acid treatment the oil is contacted with sulfuric acid and then the resulting acid sludge is separated from the oil. This process results in an acid sludge disposal problem. Phenol extraction and furfural treating are the more prominent forms of lube oil treating. Both processes use the respective solvents to separate armoatics and naphthenes form the charge oil. Other treating processes which are in use are as follows:

- Edeleanu Process - liquid SO_2/benzene solvent

- Duo-sol - propane and cresylic acid solvent

Following treatment the oils are routed to a solvent dewaxing process for removal of wax and improvement of pour point. The process involves mixing the oil with a solvent, cooling the mixture and filtering out the precipitated wax, and separating the oil from the solvent. The most prominent solvent is a mixture of methylethylketone (MEK) and benzene and/or toluene. Other solvents which are in use include propane, acetone, ethylene dichloride and benzene, and dichloroethane and methyl chloride.

The product from the solvent dewaxing unit, known as slack wax, has too high of oil content to meet marketing specifications. In order to reduce the oil content, the slack wax may be heated to "sweat" the oil out. Another method of lowering the oil content involves mixing the wax with dewaxing solvent and filtering again. This operation is known as repulping. Slack wax must usually go through the repulping process twice for the oil to be sufficiently reduced.

Oil from the dewaxing unit goes to finishing for color improvement and oxidation stability. Lube oils are finished by removal of traces of resinous materials and compounds which can potentially form organic acids. Oil is finished by either clay treating or hydrofinishing. Clay treating involves percolating the oil through a packed clay column. This process is not used on a large scale due to problems with spent clay disposal (SO-076). Hy-finishing involves hydrotreating the lube in order to remove organic nitrogen and oxygen compounds.

The finished lube oil stocks are blended in various proportions to produce the finished lube oil products. The many different lube products result from blending the several lube oil stocks and the addition of special additive packages. Bulk products may be mixed in-line prior to storage, while small volume or specialty products may be prepared in compounding vessels.

The relationship of the lube processing facilities to the other refinery processes is illustrated in Figure 2.1-4. A typical lube oil processing sequence is shown in Figure 2.1-5.

Petrochemical Refinery

Petrochemical processing operations may be a part of any basic refinery configuration. The units normally associated with refineries are an olefins plant and an aromatics plant. The olefins plant may receive a feed of light hydrocarbons (C_2-C_4) from the light ends recovery unit producing ethylene, propylene, and butadiene. Other feedstocks which may be routed to an olefins plant include naphtha and gas oil. Modern olefin plants are frequently designed for total feedstock flexibility and are therefore able to meet production demands with any rates of feedstocks (ST-221). By-products from the olefins plant are a hydrogen stream, a pyrolysis gasoline, and a pyrolysis oil. The hydrogen is normally routed to the refinery hydrotreating or hydrocracking facilities while the pyrolysis oil is sent to heavy fuel oil product tankage. Pyrolysis gasoline is normally routed to the aromatics plant.

The aromatics plant receives the pyrolysis gasoline from the olefin unit as well as any aromatic rich naphtha streams from the refinery. A major source of aromatics in the refinery is the catalytic reforming units. When an aromatics plant

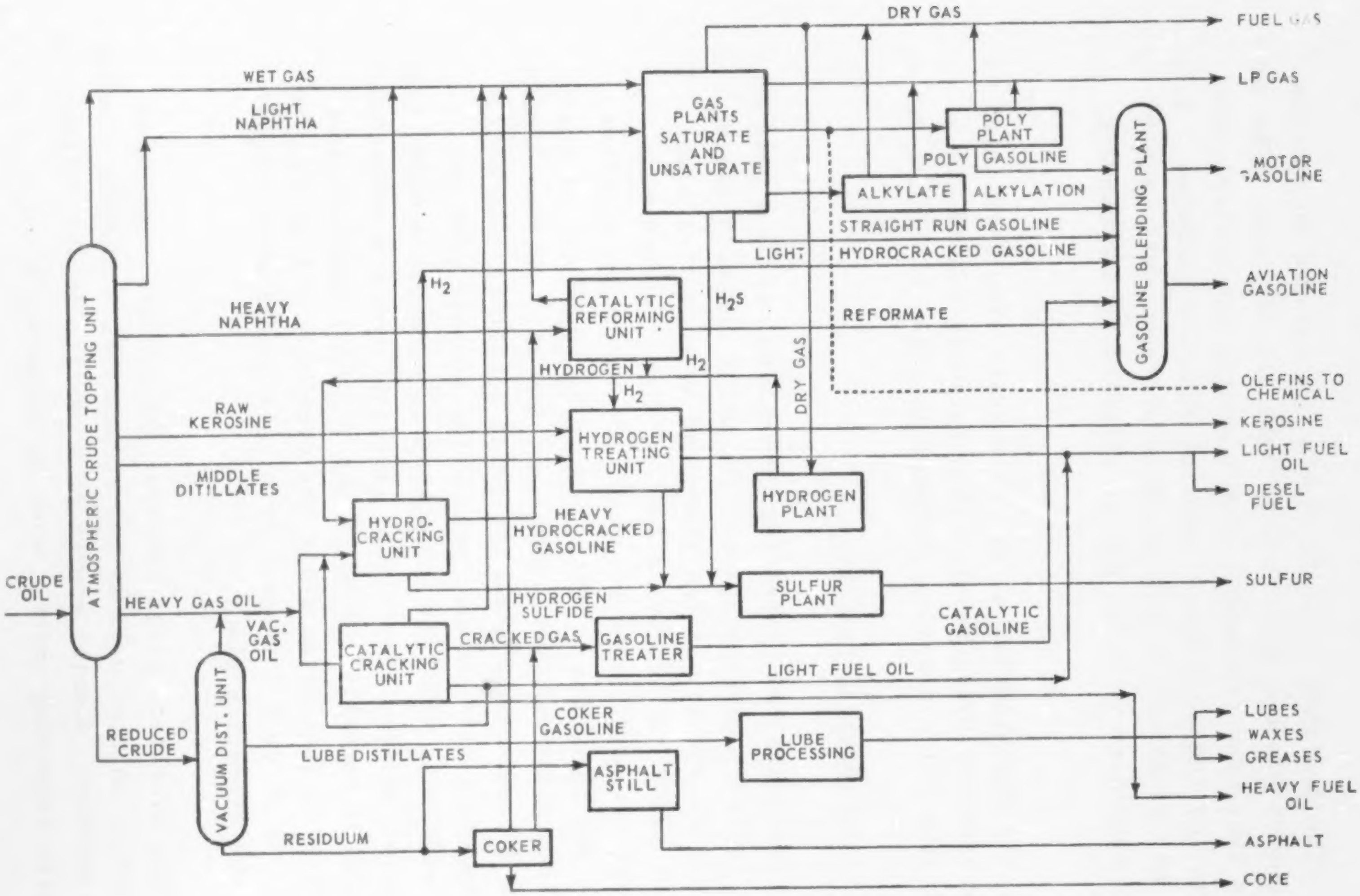

DRY GAS
FUEL GAS
WET GAS
LP GAS
LIGHT NAPHTHA
GAS PLANTS SATURATE AND UNSATURATE
POLY PLANT
POLY
GASOLINE
MOTOR GASOLINE
ALKYLATE
ALKYLATION
STRAIGHT RUN GASOLINE
LIGHT
HYDROCRACKED GASOLINE
GASOLINE BLENDING PLANT
AVIATION GASOLINE
ATMOSPHERIC CRUDE TOPPING UNIT
H_2
CATALYTIC REFORMING UNIT
H_2S
HEAVY NAPHTHA
REFORMATE
HYDROGEN
H_2
DRY GAS
OLEFINS TO CHEMICAL
H_2
RAW KEROSINE
HYDROGEN TREATING UNIT
KEROSINE
LIGHT FUEL OIL
MIDDLE DITILLATES
DIESEL FUEL
HYDROGEN PLANT
HYDRO-CRACKING UNIT
HEAVY HYDROCRACKED GASOLINE
CRUDE OIL
SULFUR PLANT
SULFUR
HEAVY GAS OIL
HYDROGEN SULFIDE
VAC. GAS OIL
CATALYTIC GASOLINE
CATALYTIC CRACKING UNIT
CRACKED GAS
GASOLINE TREATER
LIGHT FUEL OIL
VACUUM DIST. UNIT
COKER GASOLINE
LUBES
REDUCED CRUDE
LUBE PROCESSING
WAXES
LUBE DISTILLATES
GREASES
ASPHALT STILL
HEAVY FUEL OIL
RESIDUUM
COKER
ASPHALT
COKE

FIGURE 2.1-4 PROCESSING PLAN FOR TYPICAL COMPLETE REFINERY

Source: NA-032

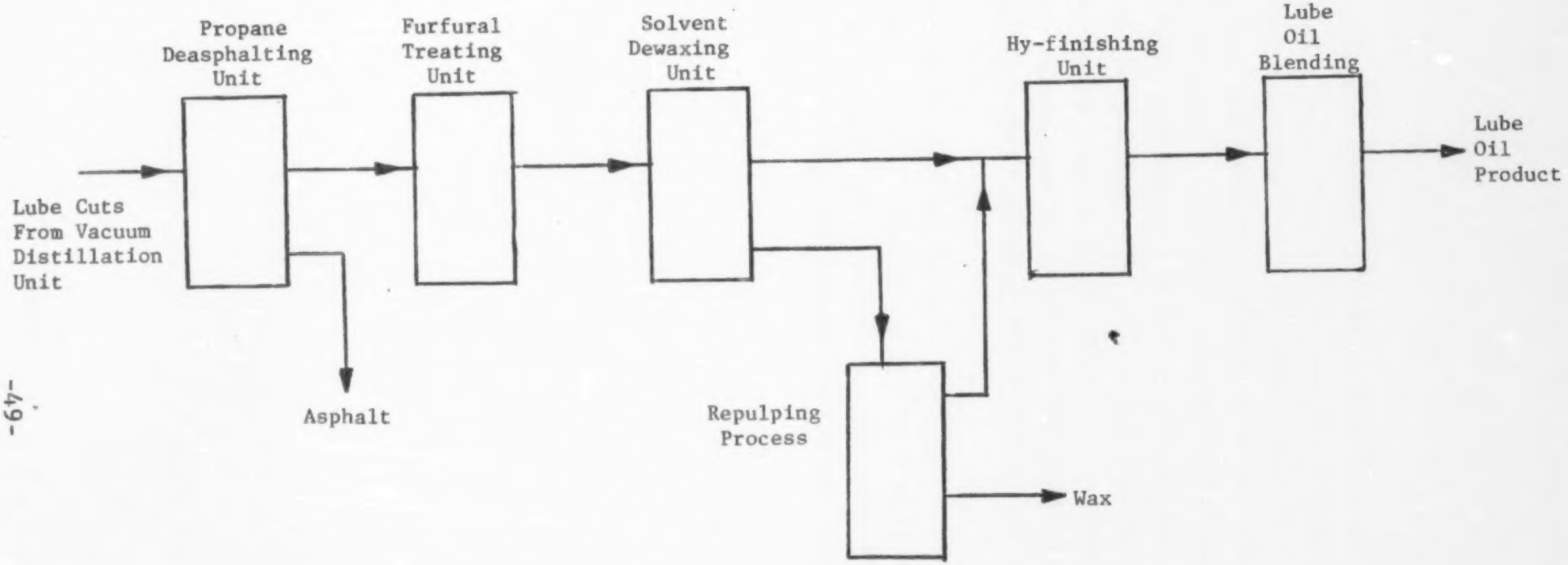

Propane
Deasphalting
Unit
Furfural
Treating
Unit
Solvent
Dewaxing
Unit
Hy-finishing
Unit
Lube
Oil
Blending
Lube
Oil
Product
Lube Cuts
From Vacuum
Distillation
Unit
Asphalt
Repulping
Process
Wax

FIGURE 2.1-5 LUBE OIL PROCESSING SEQUENCE

is included in the refinery a liquid-liquid aromatic extraction unit is used in conjunction with the catalytic reformers. The aromatic extraction unit separates the reformate stream into a raffinate stream containing the non-aromatics and an extract stream containing 95% aromatics (DE-070). Specialty cuts from other processes may be routed to the aromatics plant if the amount of aromatics makes the separation and handling of these streams economically feasible. Product streams from an aromatics plant are benzenes, toluenes, and xylenes. A non-aromatic naphtha stream is routed to the refinery gasoline blending facilities.

A simple block flow diagram of the petrochemical facilities is presented in Figure 2.1-6. These facilities may be associated with any basic refinery processing sequence (topping, fuel oil, gasoline) regardless of complexity.

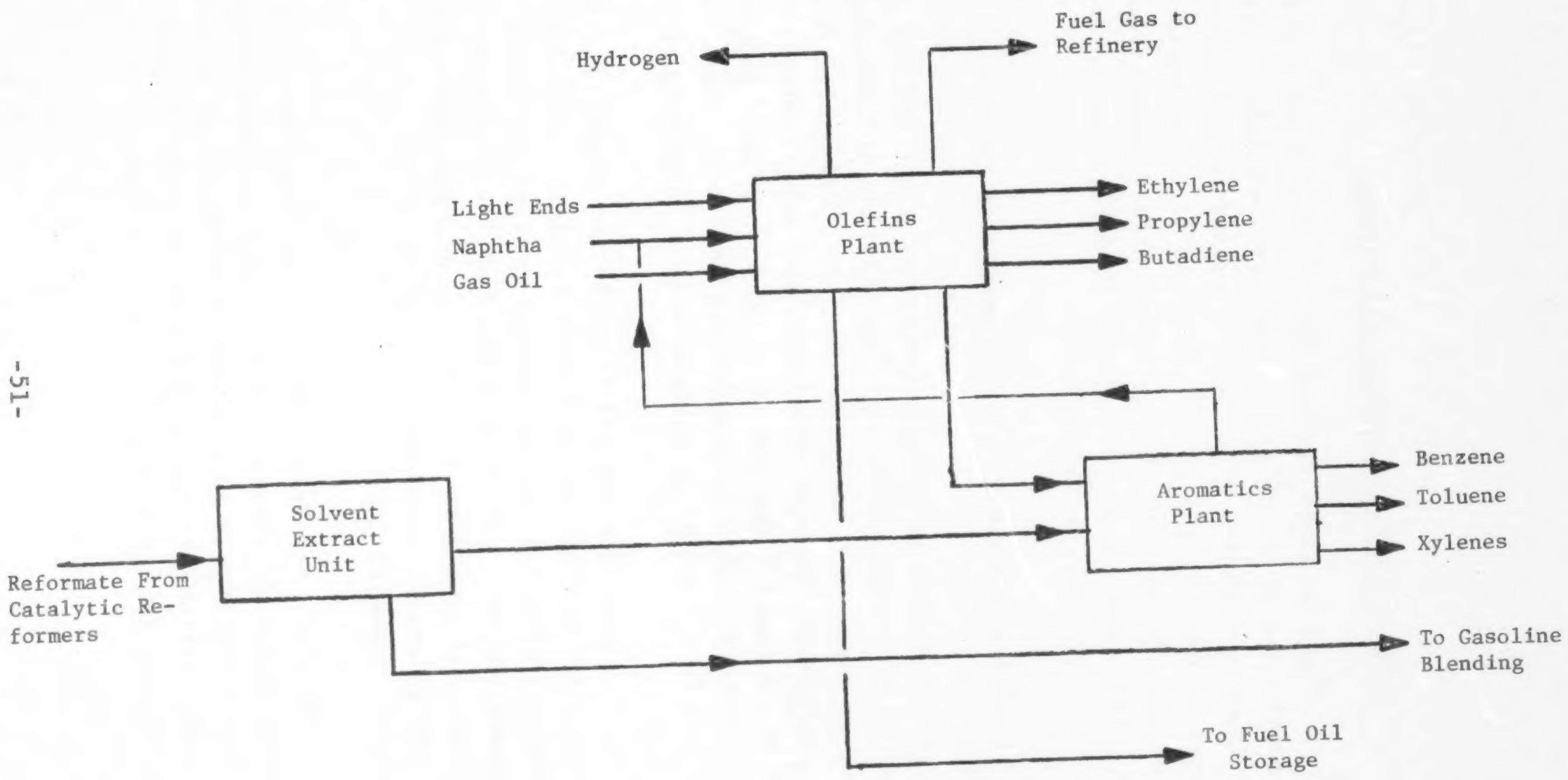

Hydrogen
Fuel Gas to Refinery
Light Ends
Naphtha
Gas Oil
Olefins Plant
Ethylene
Propylene
Butadiene
Reformate From Catalytic Reformers
Solvent Extract Unit
Aromatics Plant
Benzene
Toluene
Xylenes
To Gasoline Blending
To Fuel Oil Storage

FIGURE 2.1-6 PETROCHEMICAL PROCESSING SEQUENCE

2.2 LNG Process Technology Description

Liquefied natural gas (LNG) has enjoyed a widespread and growing use in the world in the last ten years. This growth has primarily resulted from the increasing demand for and attractiveness of natural gas as a fuel as well as the added convenience that transportation and storage of liquefied natural gas has over natural gas. One cubic foot of LNG is equivalent to over 600 standard cubic feet of natural gas.

There are numerous LNG facilities in service or under construction in the U.S. and throughout the world. Basically, two types of plants exist, the base load plant and the peak-shaving plant. Large base load liquefaction installations are located in areas such as the Middle East, Indonesia, and Alaska where significant amounts of natural gas are produced, yet very little is consumed. The gas is piped to a plant located on the coast, liquefied, and transported via LNG tanker to a regasification facility located in an area with a large natural gas demand.

The peak-shaving gas liquefaction plant is used for a different purpose than the base load facility. Its function is to liquefy natural gas during surplus periods and store it for peak demand periods. At peak demand, LNG is withdrawn from storage, regasified, and sent into the pipeline distribution grid. These plants are generally much smaller than base load operations in liquefaction capacity (LE-156).

However, regardless of the size, the basic liquefaction processing steps are similar for base load and peak-shaving plants. Figure 2.2-1 presents a generalized flow sketch of an LNG scheme. If the liquefaction facilities are near an area of large gas consumption and remote from gas production fields, as is likely

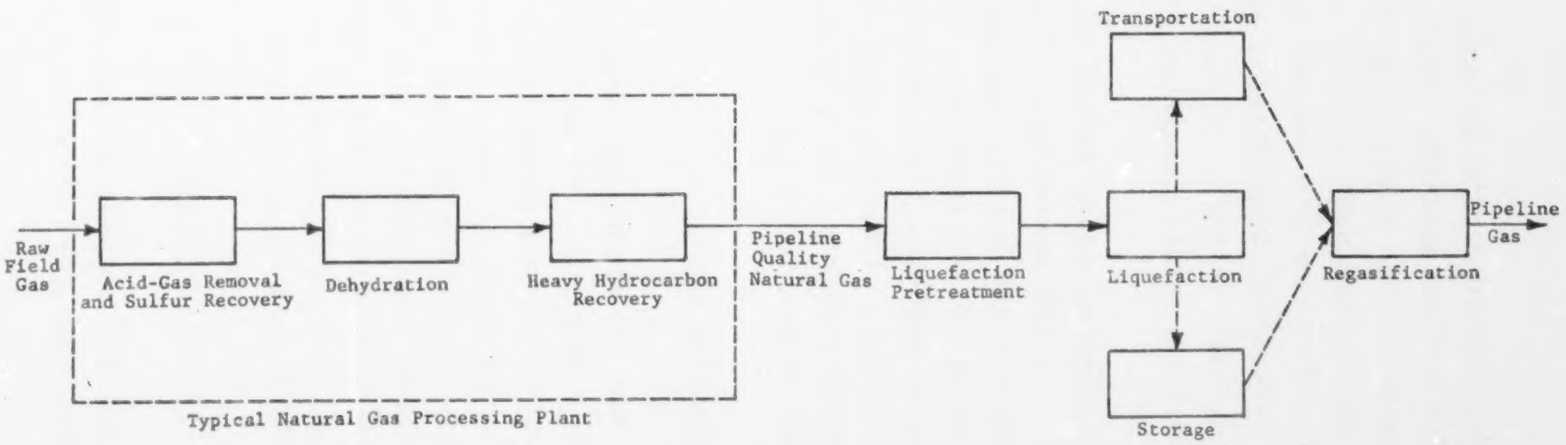

Raw Field Gas
Acid-Gas Removal and Sulfur Recovery
Dehydration
Heavy Hydrocarbon Recovery
Typical Natural Gas Processing Plant
Pipeline Quality Natural Gas
Liquefaction Pretreatment
Transportation
Liquefaction
Storage
Regasification
Pipeline Gas

FIGURE 2.2-1 GENERALIZED FLOW PLAN FOR LNG SCHEME

for peak-shaving installations, the natural gas feed to the LNG plant is usually of pipeline quality. That is to say, it has already been processed through a gas plant for the removal of impurities such as water, hydrogen sulfide, and carbon dioxide and for the recovery of ethane and heavier hydrocarbon compounds. For this reason, a section on conventional gas processing operations will not be included in the technology description of peak-shaving liquefaction plants presented in Section 2.2.1.

This processing sequence is not the usual situation encountered in base load LNG operations. Typically, the base load plant will receive a raw natural gas which requires extensive processing prior to liquefaction. This gas purification section may resemble in sequence the flow pattern presented in Figure 2.2-1 or, as is more often the case, the gas processing steps may be integrated providing for a more efficient operation. This case is dicussed in Section 2.2.2.

2.2.1 LNG Peak-Shaving Plant

There has been an increased tempo in peak-shaving plant development in recent years. By the end of 1975 there will be about fifty peak-shaving installations operating in the U.S. with a combined liquefaction capacity of over 300 million cubic feet per day. The majority of these plants are located in the north and northeastern areas of the country, with Massachusetts having the most liquefaction facilities at six. The individual plant capacities range from a low of 0.5 MM scfd to a high of 25.0 MM scfd. The average plant size is in the 5-10 MM scfd range (US-191).

2.2.1.1 Natural Gas Feed Preparation

Since the gas fed to peak-shaving liquefaction installations has been normally processed in a natural gas plant, the degree of clean up required is minimal (LO-102). Liquefaction of natural gas requires process temperatures as low as -260°F. Therefore, any constituents of the inlet gas stream that may become solid at these temperatures must be removed to the extent that they will remain in solution in the LNG to avoid significant fouling or plugging problems. The two constituents found in the gas feed to peak-shaving plants that must be so reduced are water and carbon dioxide. In addition, process requirements necessitate removal of hydrogen sulfide, should it be present (AM-127).

Permissible concentrations of impurities in natural gas feeds depend on the choice of the subsequent liquefaction process and particularly on the susceptibility to fouling and blockage of heat exchangers and expansion engines used for refrigeration. Generally it is desirable that the water content of the gas should be less than 1 ppm. Carbon dioxide concentrations should be in the range of 50 to 150 ppm. Hydrogen sulfide, as far as potential fouling is concerned, could probably be as high as 30 to 50 ppm; but in fact other considerations such as odor, corrosion and toxicity restrict it to a maximum of 3 ppm or less.

This clean up job is most often accomplished with the use of molecular sieve synthetic zeolite adsorbents (LO-102). They offer an economical and very thorough one-step CO_2, H_2O, and H_2S removal ability. Should the quantity of H_2S removed be large enough, it is recovered as sulfur in a Claus plant. A flow sheet of a typical molecular sieve process for application to a peak-shaving plant is shown in Figure 2.2-2. After physical separation of entrained solids and liquids, the incoming gas flows downward through a tower filled with molecular sieves. Water is removed in the upper section of the adsorbent bed and carbon dioxide is removed in the lower section. Effluent natural gas typically contains less than 20 ppm CO_2 and less than 1 ppm H_2O. When the tower approaches saturation, the inlet stream

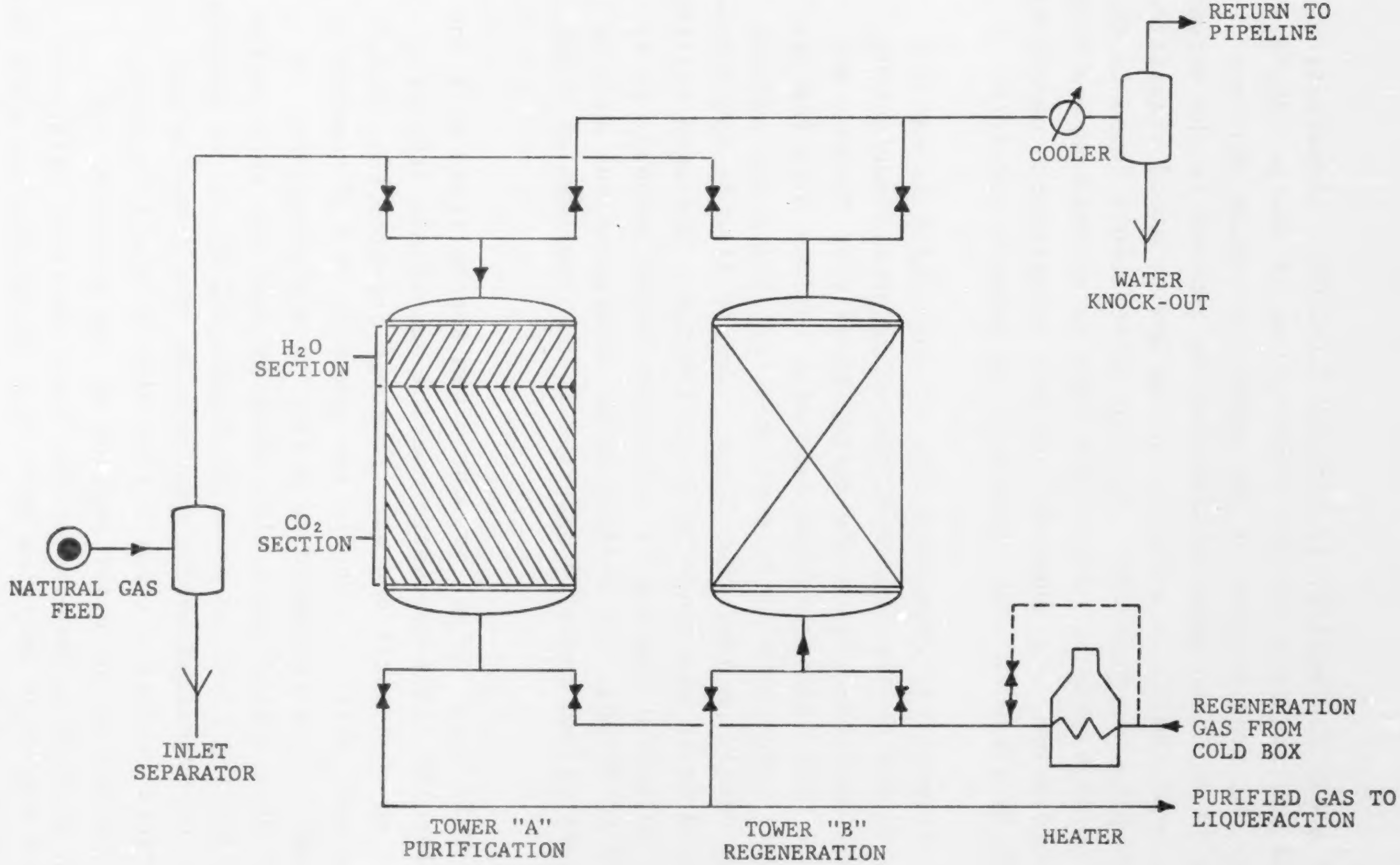

RETURN TO PIPELINE
COOLER
WATER KNOCK-OUT
H_2O SECTION
CO_2 SECTION
NATURAL GAS FEED
INLET SEPARATOR
REGENERATION GAS FROM COLD BOX
PURIFIED GAS TO LIQUEFACTION
TOWER "A" PURIFICATION
TOWER "B" REGENERATION
HEATER

FIGURE 2.2-2 MOLECULAR SIEVE SYSTEM FOR COMBINED NATURAL GAS DEHYDRATION AND CO_2 REMOVAL

SOURCE: (AM-127)

is switched to a second tower, while the adsorbent in the first is regenerated by flowing heated, dry gas counterflow to the direction of the stream that was being cleaned. After leaving the tower, the warm, moist regeneration gas is cooled and much of the water is condensed, separated, and removed from the system. The regeneration gas is then passed back to the pipeline main, mixed with the incoming gas to the adsorbing tower, or used as fuel for a boiler or prime mover (AM-127).

2.2.1.2 Liquefaction Cycles

Although there are many refrigeration cycles which can liquefy natural gas, the three types most commonly used in LNG plants are: the cascade, the mixed refrigerant, and the expander. Whether they are labeled as such, most present-day natural gas liquefaction cycles are variations or modifications of these three basic types.

Cascade Cycle

A typical cascade cycle diagramed in Figure 2.2-3 (IN-029) is a combination of vapor-compression refrigeration stages which may normally utilize three refrigerants: propane, ethylene, and methane.

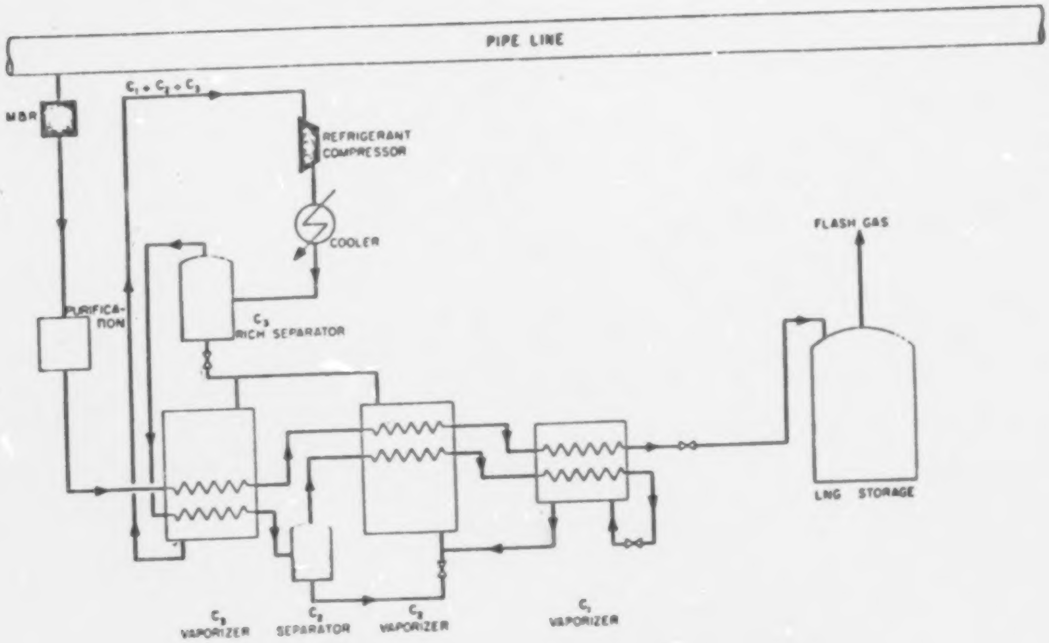
- Propane is compressed from about 15 psia to a pressure sufficient for condensation by air or water.

- Ethylene is compressed in two stages and condensed in the low-pressure propane evaporator. The propane and ethylene precool and condense the natural gas stream.

FIGURE 2.2-3

TYPICAL CASCADE CYCLE FOR NATURAL GAS LIQUEFACTION

SOURCE: IN-029)


PIPE LINE
MBR
$C_1 + C_2 + C_3$
REFRIGERANT COMPRESSOR
COOLER
PURIFICATION
C_3 RICH SEPARATOR
FLASH GAS
LNG STORAGE
C_3 VAPORIZER
C_2 SEPARATOR
C_2 VAPORIZER
C_1 VAPORIZER

- The third refrigerant, methane, is sometimes used in a closed cycle for subcooling the LNG, the methane being condensed with ethylene.

Sometimes an open cycle system is used, in which a small side stream of product LNG is recycled to subcool the liquefaction stream. A cascade cycle is usually the most thermodynamically efficient, requiring the lowest horsepower (WH-032).

Mixed-Refrigerant Cycle

The mixed-refrigerant cycle is also a vapor-compression type of cycle using air or water to condense the refrigerant. However, in this cycle, pictured in Figure 2.2-4, it is possible to obtain a low temperature with one mixed refrigerant. The need for many compressors or a multiservice compressor and many evaporators is thereby eliminated.

The simplicity of this cycle decreases the amount of control, piping, and mechanical equipment required; however, many actual mixed-refrigerant cycles are less thermodynamically efficient than the cascade cycle.

Expander Cycle

The expander cycle, shown in Figure 2.2-5, is most popular when used in parallel with an existing regulator station. An expander system uses the refrigeration available from expanding gas. This refrigeration capacity normally occurs in a distribution system where gas pressure is dropped between a cross-country pipeline and a low-pressure line. For this reason the expander cycle has found specialized application in peak-shaving liquefaction plants (IN-029).

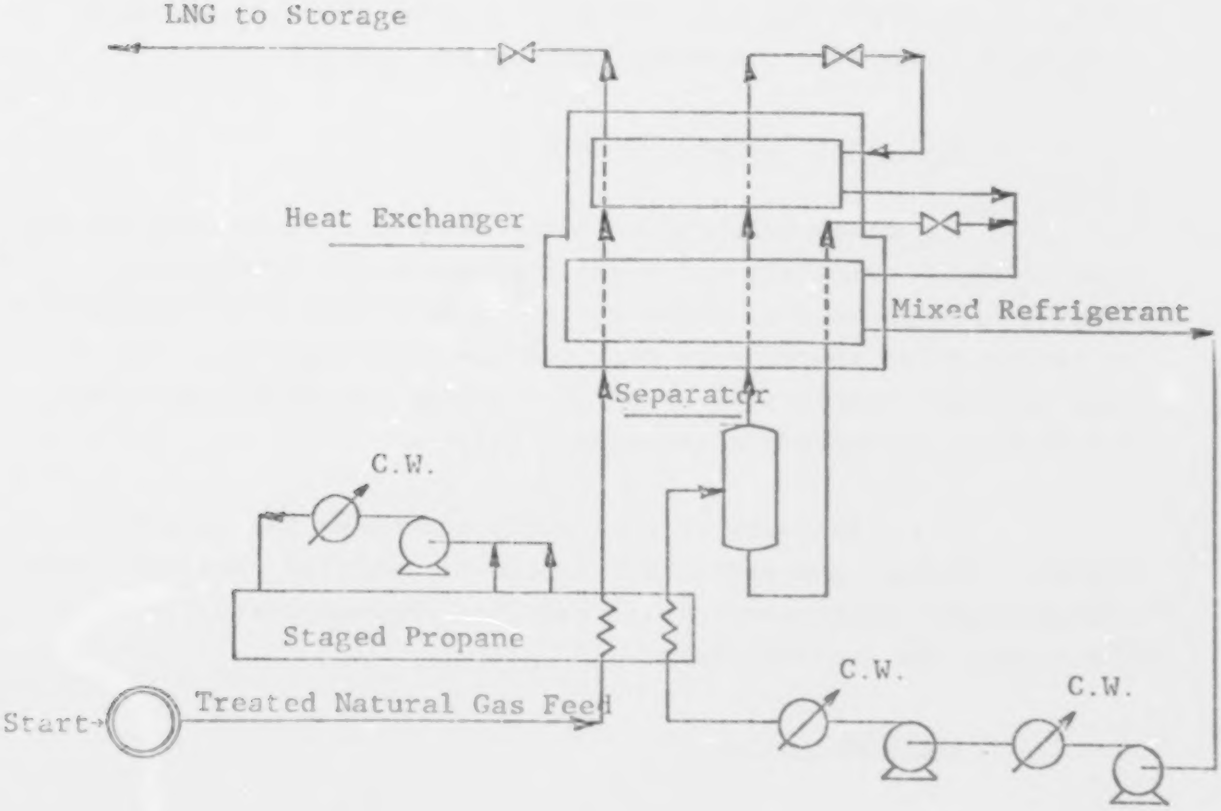

LNG to Storage
Heat Exchanger
Mixed Refrigerant
Separator
C.W.
Staged Propane
Start
Treated Natural Gas Feed
C.W.
C.W.

FIGURE 2.2-4 TYPICAL MIXED REFRIGERANT LIQUEFACTION CYCLE

SOURCE: (HY-014)

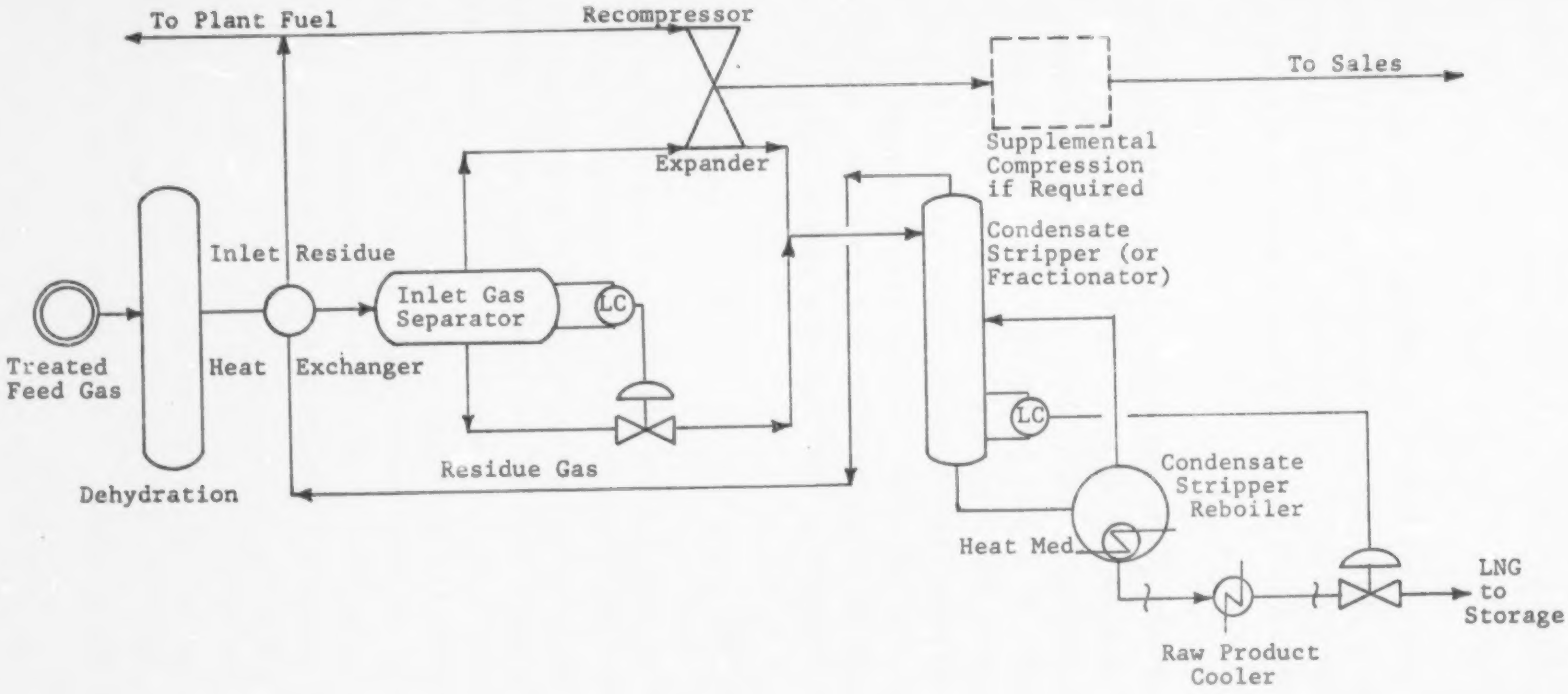

To Plant Fuel
Recompressor
To Sales
Expander
Supplemental Compression if Required
Inlet
Residue
Heat
Exchanger
Inlet Gas Separator
LC
Condensate Stripper (or Fractionator)
Treated Feed Gas
Dehydration
Residue Gas
LC
Condensate Stripper Reboiler
Heat Med.
LNG to Storage
Raw Product Cooler

FIGURE 2.2-5 TYPICAL EXPANDER LIQUEFACTION CYCLE

SOURCE: (HY-014)

In order to provide sufficient refrigeration, these facilities use a flow through the plant of 8 to 15 times the desired liquefaction rate. Therefore, a large quantity of gas must be handled, both in the gas clean up system and the cold box.

An advantage of this type of an expander cycle is that the system is relatively simple since the refrigerant can be handled in one stream. Also, little external horsepower is required. However, if there is insufficient flow from a high-pressure line to a low-pressure line, it is necessary to provide compression equipment for recycling gas in a closed loop, making this system less attractive. Other disadvantages are that large quantities of gas must be handled and areas for application (adjacent to a regulator station) are potentially limited.

2.2.1.3 Storage

Storage facilities for LNG are required whether the liquid is to be used to meet winter shortages of gas or to supply base load gas by long distance shipment. In the latter case complete ships' cargoes have to be loaded into and unloaded from LNG tankers, i.e., storage capacity must be at least equal to the maximum volume of LNG expected in any one shipment. Storage for peak shaving, on the other hand, depends on the number of days per year during which gas is to be liquefied - 200 to 220 in a temperate climate - and on the daily capacity of the liquefaction plant (LO-102).

LNG can be contained on shore in three basic types of storage facilities: the above-ground double-walled metal tanks, prestressed concrete tanks, and in-ground or cavern spaces.

Metal Tanks

All but one of the United States' peak-shaving plants uses the above-ground metal tank for storage. The popularity of this type of tankage is due to the improved control of heat leakage, easier access for repairs, and lack of geological constraints.

The embrittlement of mild steel at temperatures below -50°C makes it necessary to provide aluminum or 9% nickel-stainless steel to contain the liquid. The outer shell of these containers is carbon steel. Sandwiched between the two vessels at the bottom of the tank is a load-bearing insulation and between the walls of the tank is an insulation system such as loose-fill perlite. The roof should be covered with glass fiber or a similar lightweight insulating material. This method of construction results in a container similar to the ones used on-board LNG ships.

Other Types of Storage

There are available to the LNG industry various alternatives to the metal tank. However, to date there are few facilities which use a different storage technique.

Concrete has passed low-temperature and LNG-immersion tests and as a result can be classified a suitable construction material if correctly prepared. When used to form a large container, it must be reinforced with prestressed or poststressed rods or wire to prevent cracks resulting from thermal stresses. These storage tanks may be insulated on the outside, or inside of the concrete wall, and can be located either above or below ground (IN-029).

Cryogenic in-ground storage has been the subject of a great deal of research and study in recent years. As a result of these efforts, this storage system has been brought to the point where accurate construction estimates can be made. The container itself consists of an excavated, earthen storage cavity with no insulation and no liner. The roof may be made of either 9% nickel steel or aluminum on the inner lining, with some insulation separating this inner wall from the outside shell (IN-029).

Cavern storage presents yet another method of storing LNG. The Institute of Gas Technology has developed a large volume room and pillow storage technique which could be applicable to peak-shaving facilities. The room would be close to the surface and insulated to reduce boil off. Gaz de France has designed a large volume storage which could be utilized in base load operations. This concept consists of a vertical shaft used as an access to a large horizontal storage gallery, which is excavated in impermeable strata. The gallery is operated at a pressure corresponding to the hydrostatic pressure of the overburden (IN-029).

2.2.1.4 Regasification Systems

It has been traditional to vaporize LNG before burning it. Whether this will be necessary or desirable for future LNG-fueled power plants is open to question. Existing LNG base load, peak-shaving and peak-shaving satellite plants serve gas pipelines and, therefore, vaporization of LNG is mandatory. Fortunately, there are a variety of reliable vaporizers available and these do not represent an inordinate part of the invested capital of the LNG system. Fired vaporizers absorb approximately 2% of the heating value that they transmit to the pipeline (IN-029).

Direct-Fired Vaporizers

The direct-fired vaporizer consists of stainless steel finned tubing stacked on a rectangular chamber. LNG comes in at the bottom and leaves as a gas out the top. A hot inert gas at about $1000^{\circ}F$ flows in a dual elliptical path and maintains a heat flux of about 20,000 $Btu/hr/ft^2$ of pipe surface. The gas circulates an average of 5 times around this bank before going out the stack. The efficiency of this unit is about 70-75% and can be improved to 87% if heated air is returned to the blower (IN-029).

Submerged Combustion Vaporizers

Figure 2.2-6 illustrates the principles of the submerged combustion heat exchanger. The LNG is circulated in stainless steel tubes that are immersed in a hot water bath. High pressure fuel and air are burned in the downcomer and the products of combustion flow through the water bubbling up inside the weir.

The efficiency of this system is 90-95% based on the higher heating value of the fuel. Also, the submerged combustion system has a longer thermal reservoir than the direct-fired exchanger. This tends to provide a cushion for sudden fluctuations in demand.

Indirect-Fired Intermediate Fluid Vaporizers

Figure 2.2-7 shows a typical indirect-fired system. In this system, the LNG is vaporized and superheated in a heat exchanger with pentane. The pentane is in turn heated by a water-glycol mixture which is heated by a natural gas-fired furnace.

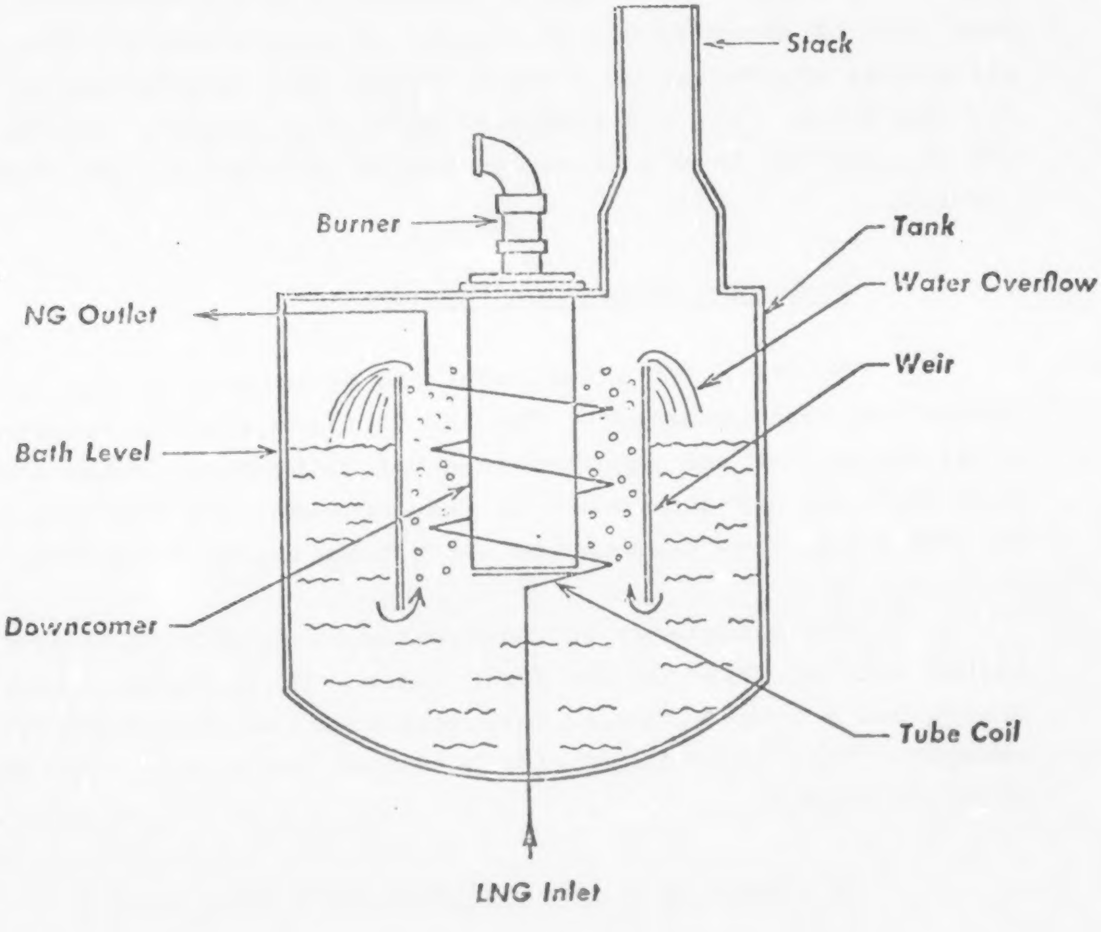

Stack
Burner
Tank
Water Overflow
NG Outlet
Weir
Bath Level
Downcomer
Tube Coil
LNG Inlet

FIGURE 2.2-6 SUBMERGED COMBUSTION VAPORIZER

SOURCE: (IN-029)

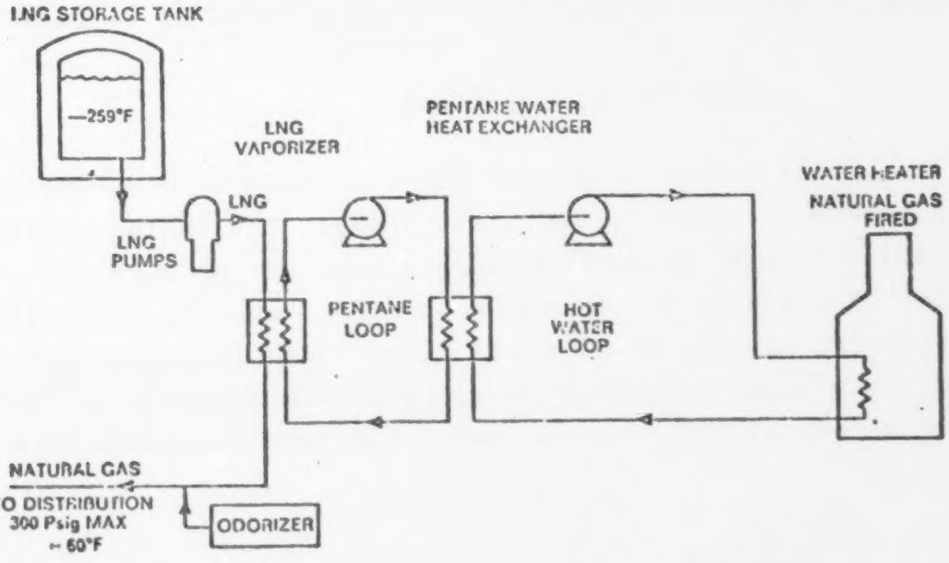

LNG STORAGE TANK
—259°F
LNG VAPORIZER
LNG
LNG PUMPS
PENTANE WATER HEAT EXCHANGER
PENTANE LOOP
HOT WATER LOOP
WATER HEATER NATURAL GAS FIRED
NATURAL GAS
TO DISTRIBUTION
300 Psig MAX
~ 60°F
ODORIZER

FIGURE 2.2-7 INDIRECT-FIRED INTERMEDIATE FLUID VAPORIZER
SOURCE: (IN-029)

Ambient Air Vaporizers

This type of vaporizer has been used in small applications, but would not be suited for the large demands of base load plants due to the low rate of heat transfer per unit area of heat exchanger. A very large surface area would be required to vaporize the LNG. Ambient air temperature, winter to summer, would have a significant effect on output. This type of exchanger uses aluminum-plate fins and special cross-section tubing to provide as much area for heat exchange as possible.

Unfired Water Vaporizers

In these vaporizers LNG is pumped into manifolds in the bottom of banks of vertical tubing. The tubing is internally finned and water flows down the outside of the tubes in a thin film. The formation of ice on the tube banks is controlled by regulating the amount of water flow. Such installations compare well with other gasification systems when utilized in connection with a coastal LNG terminal receiving tank shipments from foreign sources.

2.2.2 Base Load Plant

Base load LNG plants are based upon the economy of tanker shipment of methane in the liquid phase. Large liquefaction facilities are located in areas of abundant natural gas supply, and the corresponding regasification units are sited to serve large consumption centers.

Only a little over 10 years have passed since LNG first reached commercial status. Now LNG is the principal means of transporting excess gas from world areas where there is plenty to areas where energy is short. So far there are more than 5,000

MM scfd of capacity in operation or under construction around the world.

Table 2.2-1 illustrates that this is equivalent to nearly 10% total consumption of the United States or about 5% of world consumption. In addition to these projects, a number of others are under various stages of consideration (Table 2.2-2). In all it has been estimated that about 140,000 to 230,000 MM scfd of natural gas is available in the world for LNG movement (WA-168).

Major LNG projects can be described in terms of a number of basic component parts. One can differentiate between the components of a base load LNG project as those which are located at or near the gas field and those which are located at the receiving terminals. The components at or near the gas field are:

- gas production facilities, i.e., gas wells, field lines, measurement and control equipment, pressure reduction and initial purification facilities, and well-servicing equipment;

- pipelines from the gas field to the liquefaction plant, generally from inland or submarine fields to a suitable deep water port for ships in the 100-150,000 dwt class;

- liquefaction plant which normally includes gas purification, since frequently gas is piped impure; and

TABLE 2.2-1

LNG PROJECTS

Project	Principals	Begun	Approx. capacity, MMcfd
Algeria-U.K.	Sonatrach CAMEL British Methane	1964 Compl.	100
Algeria-France (Arzew to Le Havre)	Sonatrach CAMEL Gaz de France	1965 Compl.	50
Alaska-Japan	Phillips Marathon	1969 Compl.	160
Libya-Spain	Exxon Gaz Natural	1971 Compl.	120
Libya-Italy	Exxon ENI	1972 Compl.	330
Brunei-Japan	Shell Brunei Govt. Mitsubishi	1972 Compl.	770
Algeria-France (Skikda to Fos)	Sonatrach Gaz de France	1973 Compl.	380
Abu Dhabi-Japan	ADNOC BP Mitsui CFP Bridgestone	Under constr. (1976)	330
Algeria (Bethiova)	Sonatrach El Paso Natural Gas	Under constr. (1976)	1,000
Indonesia (Kalimantan)	Pertamina Huffco	Under constr. (1977)	550
Indonesia (Lho Seumawe)	Pertamina Mobil	Under constr. (1977)	1,200
Algeria (Skikda)	Sonatrach	Under constr.	175
Total			5,165

TABLE 2.2-2

PROPOSED LNG PROJECTS

Project	Participants	Status	Approx. capacity, MMcfd
Algeria-Europe (Bethiova)	Sonatrach Sagape	Engineering	1,550
Venezuela-Spain	Enagas	Reported under negotiation	....
Nigeria-Spain	Enagas	Reported under negotiation	....
Iran-Spain	Enagas	Reported under negotiation	....
Indonesia-U.S.	Pertamina Pacific Lighting	Mid-1979	550
Iran-U.S.	NIGC El Paso Sopex Distrigas	Early 1980s	2,000 then 3,000
Abu Dhabi-France	....	Proposed	....
China-Japan	Bridgestone	Reported under consideration	800
Alaska/U.S. Mainland	Pacific Lighting	Under consideration	3,800

- liquid storage of sufficient capacity to load ships without causing delay.

Those components located at the receiving terminal include:

- a suitable harbor for handling the LNG tankers,
- storage tanks for LNG large enough to receive entire ships' cargo without causing delay,
- regasification facilities for the LNG, and
- connecting pipelines with pressure regulators, measuring equipment, odorizers, etc., to connect the terminal with existing gas systems.

The following sections discuss those components of base load liquefaction plants which were not covered in the peak-shaving LNG sections. The technology review will include complete gas clean-up operations, heavy hydrocarbon recovery, and LNG transportation via tanker.

2.2.2.1 Natural Gas Conditioning and Purification

Natural gas supplied by pipeline to a base load liquefaction plant from fields situated within about 100 miles of the plant is as a rule only purified at the wellhead to a minimal extent. This means that water, acidic gas, i.e., carbon dioxide and hydrogen sulfide, higher hydrocarbons and other impurities such as dirt or entrained oil droplets may be present in the liquefaction feed.

Before natural gas can be liquefied, these contaminants must be removed, since they would solidify on cooling and plug the piping or foul the heat exchangers.

Liquid Separation

The first stage of any gas conditioning operation will consist of a trap for the collection of liquid products present in the feed to the liquefaction plant (LO-102). Depending on ambient temperature, water content of the gas, and pressure drop, glycol or methanol may be injected as an antifreeze. If this is done, glycol or methanol recovery from the aqueous layer on the gas/liquid separator will be required. This usually involves fractionation in a small atmospheric distillation plant.

After reduction of liquid water, glycol and heavier hydrocarbons by simple gas/liquid separation, the gas is cooled by heat exchange to a temperature near freezing. At pipeline pressure, this results in further condensation, and additional water and heavy hydrocarbons separate out in a knock-out drum.

Acid Gas Removal

The process which follows next in gas processing is generally referred to as gas sweetening and serves to remove both H_2S and CO_2. The acid gases present in the natural gas have a limited solubility in LNG. Their concentrations have to be reduced to avoid freezing-out in the liquefaction unit, and consequently plugging or fouling of the heat exchangers and piping. Carbon dioxide removal to levels of 50 ppm and less is essential, and H_2S removal to even lower concentrations is required of the pretreatment facilities for an LNG installation.

There exist two basic methods for combined CO_2/H_2S removal - dry or wet systems. The dry system that is used by the LNG industry is the molecular sieve. Its major advantage over the wet sweetening systems is the degree of clean-up achievable as well as simultaneous dehydration. For a description of this system see Section 2.2.1.1 on the peak-shaving clean-up discussion.

The wet sweetening systems can operate by two basically different mechanisms, i.e., a reversible chemical reaction may take place between the acid gas and the solvent, or alternatively the acid gas may merely dissolve in the absorber liquid, in preference to and generally at a faster rate than the other gas components.

Typical chemically reactive solvents include aqueous solutions of most alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), di-isopropanolamine (Adip), triethanolamine (TEA), and anthraquinone disulphonic acid (Stretford solution). In all these extractions, with the exception of the Stretford process, acid gases are absorbed at near ambient temperature by the alkaline compound and are released by heating to near its boiling point. Figure 2.2-8 shows a typical amine treating unit. The Stretford solution, on the other hand, also contains sodium vanadate, sodium carbonate and a trace of chelated iron. When blown with air, H_2S is oxidized to elemental sulfur, which can be removed by filtration.

A series of absorption solvents based on potassium carbonate act in similar fashion to the alkanolamines. In the

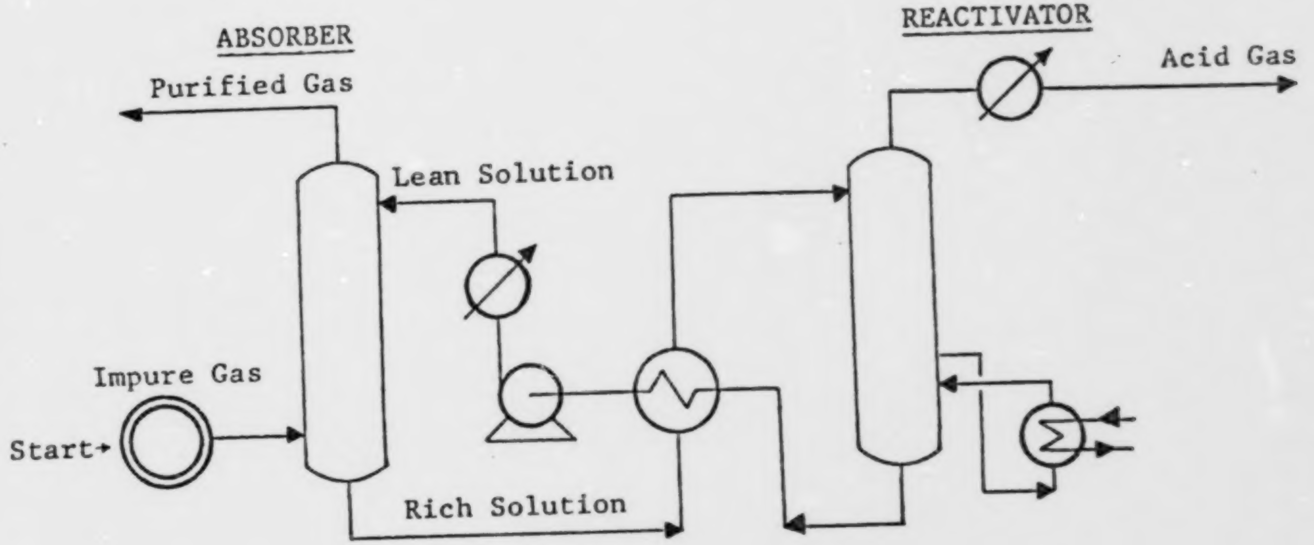

ABSORBER
Purified Gas
Lean Solution
REACTIVATOR
Acid Gas
Impure Gas
Start→
Rich Solution

FIGURE 2.2-8 TYPICAL AMINE TREATING UNIT

SOURCE: (HY-014)

Benfield, Vetrocoke, and Catacarb processes, carbon dioxide reacts with potassium carbonate to form bicarbonate, which decomposes at elevated temperatures. A similar reaction takes place with H_2S. Various additives, frequently arsenates, accelerate H_2S removal by forming thioarsenates, which decompose into arsenates and elemental sulfur (Giammarco Vetrocoke process). Catacarb and Benfield additives assist the rate of gas absorption by accelerating hydration of CO_2 gas.

Physical absorbents for acidic gases include anhydrous propylene carbonate (Fluor solvent), N-methyl-pyrrolidone (Purisol), and the dimethyl ether of polyethylene glycol (Selexol). In certain instances physical absorbents need not be heated but can be flashed at reduced pressure to release the absorbed acidic gases. Their main disadvantage, compared with chemical absorbents, is their tendency to remove higher hydrocarbons from the gas, which is particularly undesirable where sulfur is to be recovered from the acid gas in a Claus plant.

Another disadvantage of chemical absorption is the highly corrosive nature of both absorbents and, particularly, absorbent-acid compounds. In an attempt to find an acceptable compromise, hybrid processes have been developed such as the Sulfinol extraction process which uses a mixture of the physical solvent sulpholane and chemical absorbents of the alkanolamine type.

Typical operating conditions for a number of reactive solvents are listed in Table 2.2-3. A number of other solvents, both chemically reactive and physically absorbent, have been proposed and used commercially to sweeten natural gases from various sources. However, the above-mentioned processes account for the bulk of modern gas purification plants. It should be noted from Table 2.2-3 that while most processes adequately

TABLE 2.2-3

GAS SWEETENING PROCESSES

Process	Solvent	Type		Typical concentrations				
		Chem.	Phys.	Initial			Residual (ppm)	
				H_2S		CO_2	H_2S	CO_2
Adip	Di-isopropylamine	X		Bulk*		-	0.5	-
Benfield	Activated K_2CO_3	X		$H_2S/CO_2>1$		Bulk	30	150
Catacarb	Activated K_2CO_3	X		$H_2S/CO_2>1$		Bulk	30	150
Econamine	Diglycolamine	X			3-20 vol %		0.5	1,000
Fluor	Propylene carbonate		X	Bulk		Bulk	0.5	1,000
Girbotol	MEA	X		1-3 vol %			0.5	1,000
	DEA or TEA				3-10 vol %		1-2	1,000
Purisol	N-methylpyrrolidone		X	Bulk		Bulk	0.5	3,000
Selexol	Dimethoxypolyglycol		X	Bulk		Bulk	0.5	3,000
Stretford	Anthraquinonedisulphonic acid, Na_2CO_3, As_2O_3, Na_2VO_4, chel. Fe compound	X		<0.5%		Any	0.5	-
SNPA	Modified DEA	X		Bulk		Bulk	0.5	1,000
Sulfinol	Sulpholane, alkanol-amine	Hybrid		Bulk		Bulk	0.5	3,000
Vetrocoke (CO_2)	K_2CO_3, As_2O_3	X		-		Bulk	-	1,000
(H_2S)	Na_2CO_3, As_2O_3	X		>1.0%		-	5	-

*Predominant component in the gas

SOURCE: (IN-029)

remove H_2S, none accomplish a thorough enough job of CO_2 removal prior to liquefaction. Therefore, it would be necessary to have a molecular sieve as a final pretreatment of the natural gas before it is liquefied.

Dehydration

After removal of acidic impurities by means of a chemically reactive solvent, the gases are generally saturated with water (LO-102). Water vapor is probably the most common undesirable impurity in natural gas streams. It is not the water vapor itself that is objectionable, but rather the liquid or solid phase that may precipitate from the gas when it is compressed or cooled. Liquid water almost always accelerates corrosion, and ice or solid hydrates can plug valves, fittings, and even gas lines. To avoid these problems and those related to actual ice formation in the cold box of an LNG plant, it has been determined that water concentrations in the incoming gas should be reduced to 1 ppm (IN-029).

This dehydration is usually accomplished in one of two ways at a base load LNG plant. The wet gas may first be passed to a glycol unit which is followed by a small molecular sieve system or it may be dehydrated in one step by passage through a large molecular sieve system.

In the flow diagram of a typical glycol dehydration plant pictured in Figure 2.2-9, water vapor is continuously absorbed from the process gas stream by countercurrent contact with a high concentration glycol solution in a packed or bubble tray column. The dried gas passes out the top of this column, with the dilute glycol passing to a regenerator section where the glycol is concentrated to levels as high as 99.8 percent.

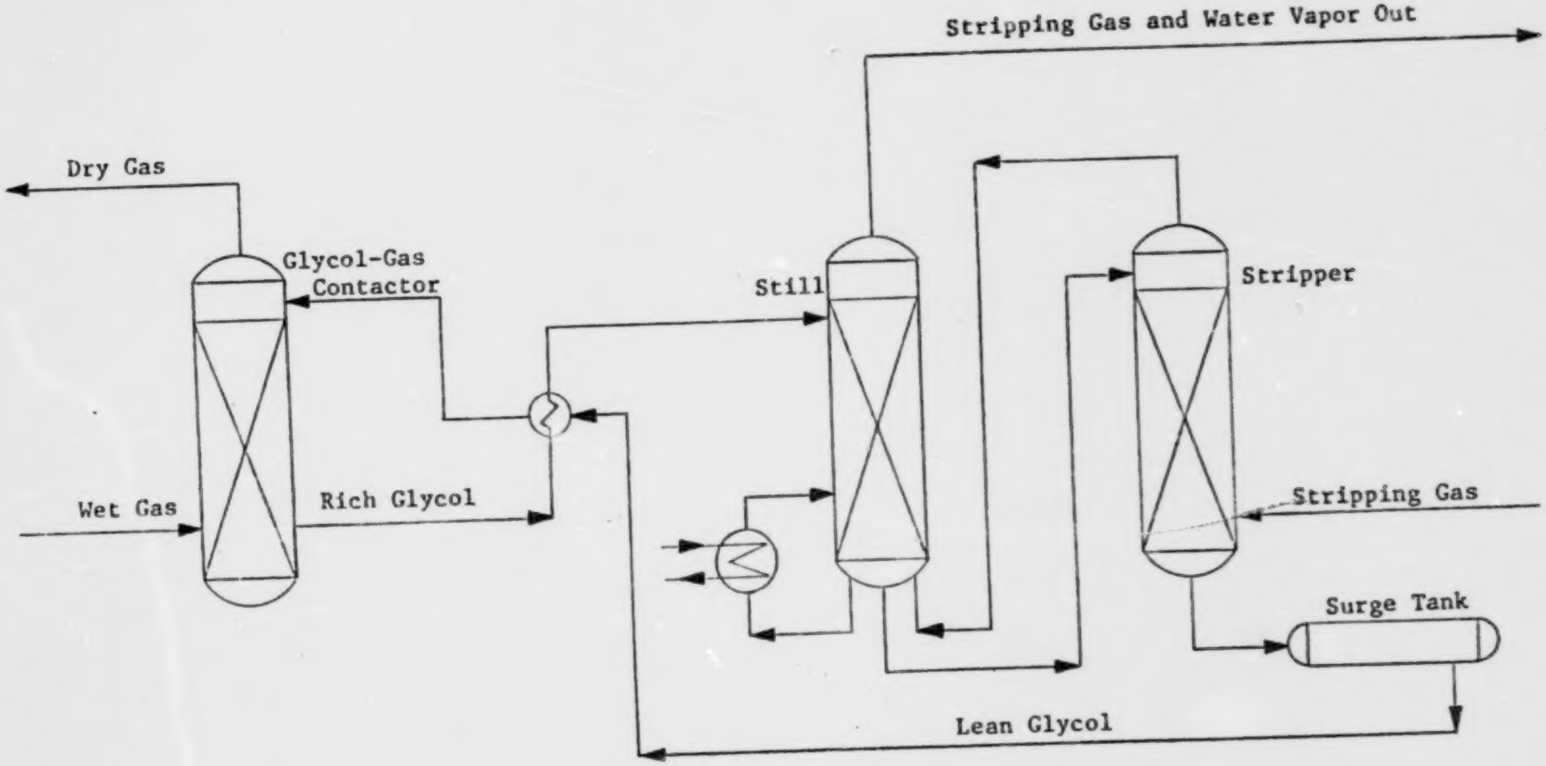

Stripping Gas and Water Vapor Out
Dry Gas
Glycol-Gas
Contactor
Still
Stripper
Wet Gas
Rich Glycol
Stripping Gas
Surge Tank
Lean Glycol

FIGURE 2.2-9 TYPICAL GLYCOL DEHYDRATION UNIT

SOURCE: (HY-014)

There are other dry dessicants available besides the molecular sieve for dehydration of the natural gas. However, for such reasons as a high sensitivity to poisoning, decline in rated capacity with pressure, and relatively short life, these systems do not appear attractive for LNG application (IN-029).

Sulfur Recovery

A means of disposal of the sulfur compounds separated in the acid gas removal units is needed in a base load LNG plant. A Claus sulfur recovery plant can provide an efficient means of converting the removed sulfur compounds to elemental sulfur for disposal.

The original technique for conversion of H_2S to sulfur was the Claus-Chance Process. It has been modified considerably in recent years. In fact, the Mathieson Chemical Company has developed a considerably improved process which has been used successfully in quite a few modern installations. A flow diagram of the modified Claus-Chance used in the Mathieson Process is shown in Figure 2.2-10.

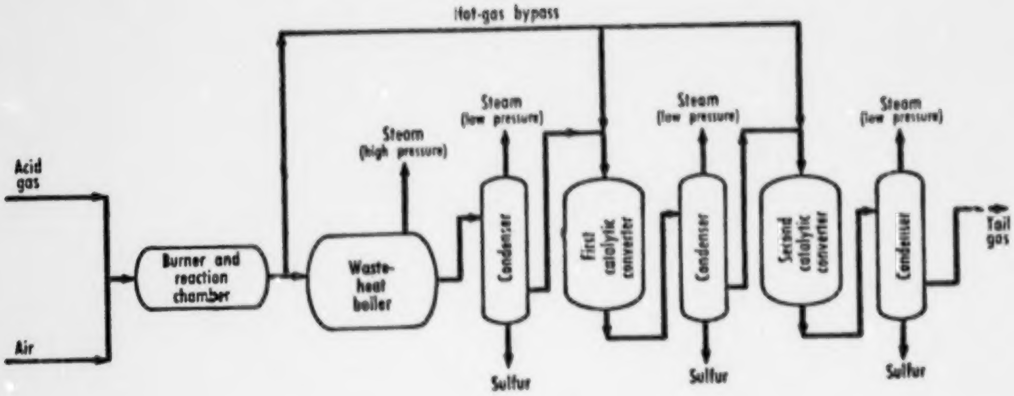
The first step consists of burning the feed gas in a specially designed reactor furnace. Flue gases from this furnace are partially cooled in a waste heat boiler and then run to a catalyst converter. After passing through the first stage of the converter the gases are run to a boiler feed water economizer and then back through the second stage of the converter.

The final step is to pass the gases into a wash tower where they are cooled and the sulfur is condensed by direct contact with a recirculated stream of liquid sulfur. Exit gases from the tower are primarily N_2, CO_2, and water vapor with some SO_2, H_2S, COS, and CS_2.

FIGURE 2.2-10

CLAUS SULFUR RECOVERY UNIT

SOURCE: (IN-029)


Hot-gas bypass
Acid gas
Air
Burner and reaction chamber
Steam (high pressure)
Waste-heat boiler
Steam (low pressure)
Condenser
Sulfur
First catalytic converter
Steam (low pressure)
Condenser
Sulfur
Second catalytic converter
Steam (low pressure)
Condenser
Sulfur
Tail gas

Sulfur removal efficiencies are dependent on the hydrogen sulfide concentration in the acid gas fed to the unit, the number of catalytic stages and the quality of the catalyst used. They can range from 90 to 98 percent.

Under the conditions prevailing in the reaction furnace, formation of some carbonyl sulfide (COS) and carbon disulfide (CS_2) is inevitable if the acid gas contains CO_2 and hydrocarbons. Although the amounts of COS and CS_2 formed are relatively small, especially if the hydrocarbon content of the acid gas is low, they are significant as potential air pollutants. A special catalyst may be placed in one or several of the catalyst converters to largely hydrolyze COS and CS_2 to H_2S and CO_2, and thus prevent CS_2 and COS from escaping into the atmosphere (IN-029).

2.2.2.2 Heavy Hydrocarbon Stripping

Heavy hydrocarbons are recovered from natural gas streams for both economic and operational reasons. The heavy hydrocarbon components of a gas may be worth considerably more when condensed and sold as a liquid than when sold as a gas. Another reason for recovery is that the presence of even small amounts of liquids in a pipeline can easily reduce the efficiency of gas flow by 10%, since liquids increase the pressure drop required for a given flow rate. Also, the presence of heavy hydrocarbons in the natural gas entering a liquefaction unit can result in freeze-ups in the heat exchangers or require inclusion of additional liquid separators and special piping in the cold box to remove these materials from the process gas stream.

Molecular sieves and other solid adsorbents offer one method for the removal of heavier hydrocarbons from natural gas streams. However, they have a much smaller capacity for adsorbing hydrocarbons than they have for water vapor. Therefore, these types of heavy hydrocarbon recovery units are seldom used in LNG plants.

Refrigerated Absorption

Refrigerated absorption offers an economical means of recovering ethane, propane, and higher components in a natural gas stream. This type of plant can theoretically achieve desired recoveries at any practical temperature and pressure by circulating the required amount of absorption oil.

As can be seen in Figure 2.2-11, high pressure natural gas, after drying and acid-gas removal, flows to a demethanizing absorber operated at essentially feed pressure. In the absorber, the feed gas is contacted with refrigerated absorption oil which can be composed of natural gasoline components recovered from the gas itself or some other hydrocarbon oil.

Rich oil from the bottom of the absorber is sent through heat exchangers to a stripper for regeneration. Light components are removed from the rich oil in the stripper by having the oil countercurrently contact open steam. The overhead product from the still is condensed and separated from water. This condensate is then fractionated in a distillation column to recover the individual components ethane, propane, butane, and the stabilized natural gasoline.

High recoveries of ethane using this process are uneconomical, due to the large steam requirement and amount of oil that must be circulated. Yet it is a favorable process for LNG remote locations since the refrigerant (propane) and the absorption oil (natural gasoline) can be recovered from the feed gas itself.

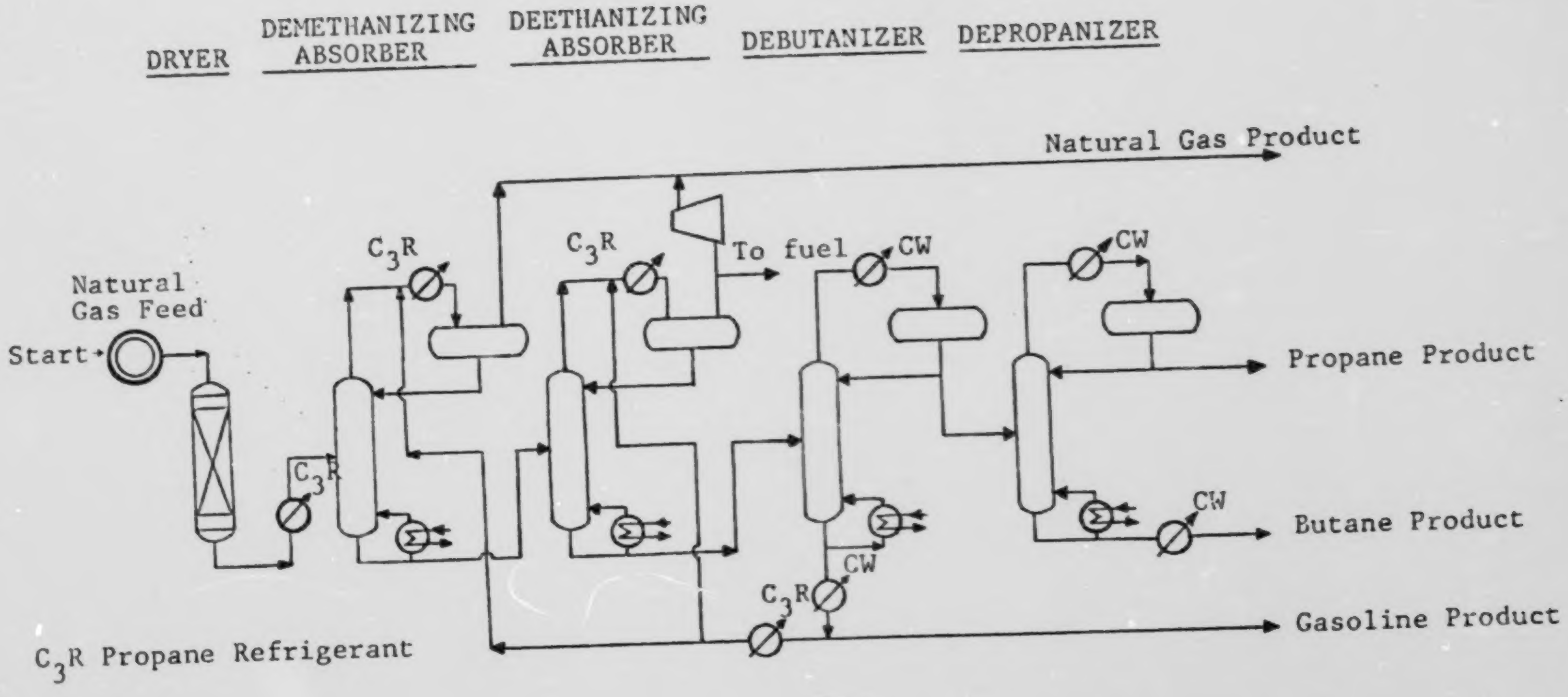

DRYER
DEMETHANIZING ABSORBER
DEETHANIZING ABSORBER
DEBUTANIZER
DEPROPANIZER
Natural Gas Product
Natural Gas Feed
Start
C_3R
C_3R
C_3R
C_3R
To fuel
CW
CW
CW
CW
Propane Product
Butane Product
Gasoline Product
C_3R Propane Refrigerant

FIGURE 2.2-11 REFRIGERATED ABSORPTION FOR RECOVERING HEAVY HYDROCARBONS

SOURCE: (HY-014)

Low Temperature Fractionation

This method of heavy hydrocarbon recovery can be efficiently utilized in an LNG plant. Figure 2.2-12 shows the flow diagram for this technique of recovery. The natural gas is cooled to a point where all the C_2 and higher components have liquefied and then fractionated in a tower designed for separating the methane from these liquefied heavier hydrocarbons. The final natural gas liquefaction process used has little or no effect on the hydrocarbon recovery.

The recovered heavy hydrocarbons are usually used as make-up refrigerant for the cold box and for plant fuel.

2.2.2.3 Liquefaction Cycles

Those liquefaction cycles presented in Section 2.2.1 of the peak-shaving technology discussion, with the exception of the expander cycle, are used in LNG base load plants as well.

2.2.2.4 Storage

The storage facilities used at the base load plant, as well as at the receiving terminal, are usually double-walled metal tanks. See the section on storage in the peak-shaving discussion for a description of the storage alternatives available.

2.2.2.5 Transportation

In base load LNG operations where natural gas is liquefied for export from countries with a surplus to areas deficient in gas, the LNG is pumped from storage, through deep-water loading facilities, to ocean-going vessels suitable for the long

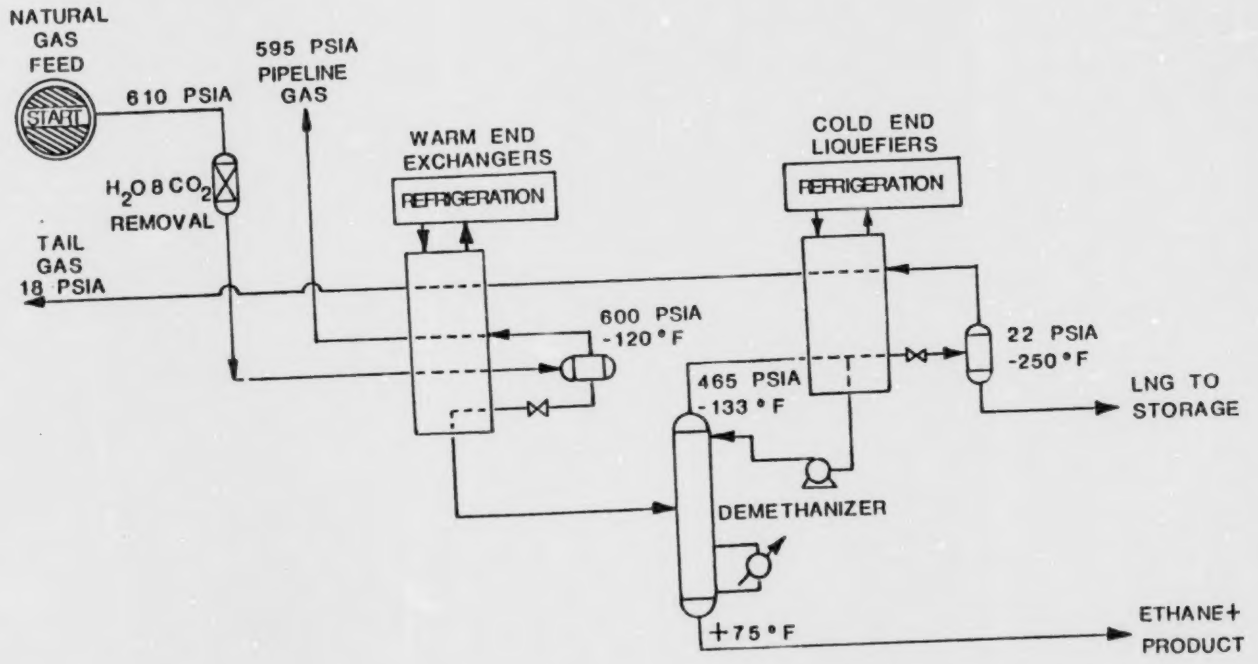

NATURAL GAS FEED
START
610 PSIA
H_2O & CO_2 REMOVAL
TAIL GAS 18 PSIA
595 PSIA PIPELINE GAS
WARM END EXCHANGERS
REFRIGERATION
600 PSIA -120 °F
COLD END LIQUEFIERS
REFRIGERATION
465 PSIA -133 °F
22 PSIA -250 °F
LNG TO STORAGE
DEMETHANIZER
+75 °F
ETHANE+ PRODUCT

FIGURE 2.2-12 LOW TEMPERATURE FRACTIONATION

distance transport of such a specialized cargo. A typical capacity for ships of current design is the equivalent of about 2,000 MM SCF.

The LNG tankers differ from other ships in the design and construction of their cargo tanks, accommodation for a vapor reliquefaction unit, and use of vaporized cargo as fuel (LO-102). Very careful design of the cargo tanks and their surroundings is essential. Two basically different methods which have been used are the construction of self-supporting or free-standing LNG tanks or the use of the hull as support for insulating layers and gas-impermeable membranes. Either type effectively provides the safety of a double hull.

The principles involved in reliquefaction of LNG vapor on board a ship are the same as those of the full-scale shore liquefaction plant, but there exist minor differences. High liquefaction performance and plant efficiency are normally sacrificed in shipboard equipment in favor of low weight and plant size. Reciprocating machinery is used, partly because of the smaller gas volumes to be compressed and also for reasons of flexibility (LO-102).

While it is possible to reliquefy all the gas vaporized by heat leakage into the LNG tanks, and this is in fact essential when the ship is loaded with LNG and stationary, there are alternative means of vapor disposal. In particular, the ship's propulsion engines and auxiliary boilers can be run on methane, whether they are of the steam turbine or diesel type. This is the case provided that the boil-off gas is pressurized and preheated before combustion and that provision has been made for dual combustion in the equipment (LO-102).

2.2.2.6 Regasification

After the LNG has been unloaded from the tanker into the receiving terminals storage facilities, it is regasified and injected into a pipeline distribution main. This operation will be a continuous operation unlike the regasification at peak-shaving plants where it occurs only to meet high gas demand. Section 2.2.1 describes those alternatives available to base load receiving terminals.

2.2.3 Satellite LNG Facilities

A particular form of peak-shaving plant is the so-called satellite LNG facility. This generally consists of a storage tank, a vaporizer, and odorization equipment. The tank is filled by truck, rail, or barge transportation of LNG from a peak-shaving liquefaction plant. Several satellites can be supplied from one central liquefaction plant (LO-102). Satellite LNG plants usually operate unattended, the flow of LNG to the vaporizer being regulated by the gas pressure in the distribution grid.

In addition to their function as peak gas producers, satellites can also be used to distribute gas in new areas which are not connected to the main supply system. Under these circumstances, a local LNG tank is filled regularly from the central tankage throughout the year.

2.3 SNG Production Technology

Synthetic natural gas (SNG) from liquids may be produced using either of two basic feedstocks, crude oil or a light petroleum such as naphtha. The official policy of the Federal Energy Administration, however, is to discourage manufacture of SNG from oil as an inefficient (8-10% energy loss), uneconomic use of resources (FE-085). The production of SNG from light petroleum derivatives such as LPG and NGL is also discouraged. As a result, the 13 SNG plants that are currently operating or under construction in the U.S. plan to use light naphtha as a feedstock or switch from a light petroleum derivative to naphtha. It is estimated that plants producing SNG from crude oil will not be utilized in the United States in the near future. For this reason the SNG technology addressed in this section applies to processes employing a light naphtha feedstock (360-370°F boiling end point).

2.3.1 Processing Steps

The preferred method of producing SNG from naphtha in large quantities is catalytic gasification followed by methanation. The basic process is available from the British Gas Council (CRG - Catalytic Rich Gas Process), Japan Gasoline Co. (MRG - Methane Rich Gas Process), or BASF/Lurgi (Gasynthan Process), either directly or through their licenses. Each of these companies is currently operating gasification processes in a number of commercial plants. The four basic steps in the process are shown in Figure 2.3-1. These processing steps are desulfurization, gasification, methanation, and purification (carbon dioxide removal and dehydration).

Desulfurization

The sulfur content in the naphtha feedstock to an SNG plant can range anywhere from one ppm to 1000 ppm (BR-103).

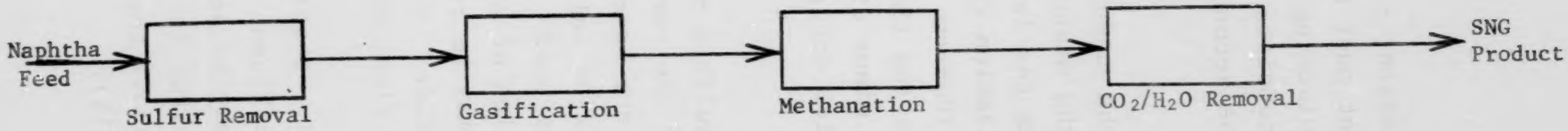

Naphtha Feed
Sulfur Removal
Gasification
Methanation
CO2/H2O Removal
SNG Product

FIGURE 2.3-1 SNG PLANT PROCESSING SFQUENCE

Since sulfur compounds represent a poison to the gasification catalyst, the sulfur content must be lowered to 0.2 ppm to avoid any significant catalyst poisoning. Desulfurization is accomplished in two stages: the first consists of catalytic conversion of sulfur compounds to H_2S; the second involves removal of the H_2S from the naphtha.

After vaporizing the naphtha feed and mixing it with a recycled hydrogen stream, the mixture of vaporized feedstock and recycled hydrogen containing gas is heated to about 650-700°F and passed over a desulfurization catalyst. The active ingredient is generally nickel-molybdenum. Organic sulfur compounds in the feedstock, mercaptans and thiophenes, are converted to H_2S. Olefin saturation and minor cracking occur. Some methanation of carbon oxides may also occur, depending upon the characteristics of the catalyst.

After the organic sulfurs have been converted to H_2S, two process alternatives for the removal of the H_2S exist. In one case, the treated gases are passed over a bed of zinc oxide which absorbs H_2S and forms zinc sulfide. Besides zinc oxide, less costly iron oxide can be used. However, during upset conditions, when the concentration of hydrogen is unusually high, iron oxide and iron sulfide may be reduced to metallic iron, with release of hydrogen sulfide. Therefore, a bed of zinc oxide is generally used as a final step.

The second alternative available for the removal of the H_2S is to route the reactor effluent to a stripper or fractionator where the sour gas may be separated. The naphtha product containing 0.2 ppm sulfur is taken from the bottom of the stripper. Figure 2.3-2 shows the steps involved in this type of desulfurization (RA-119).

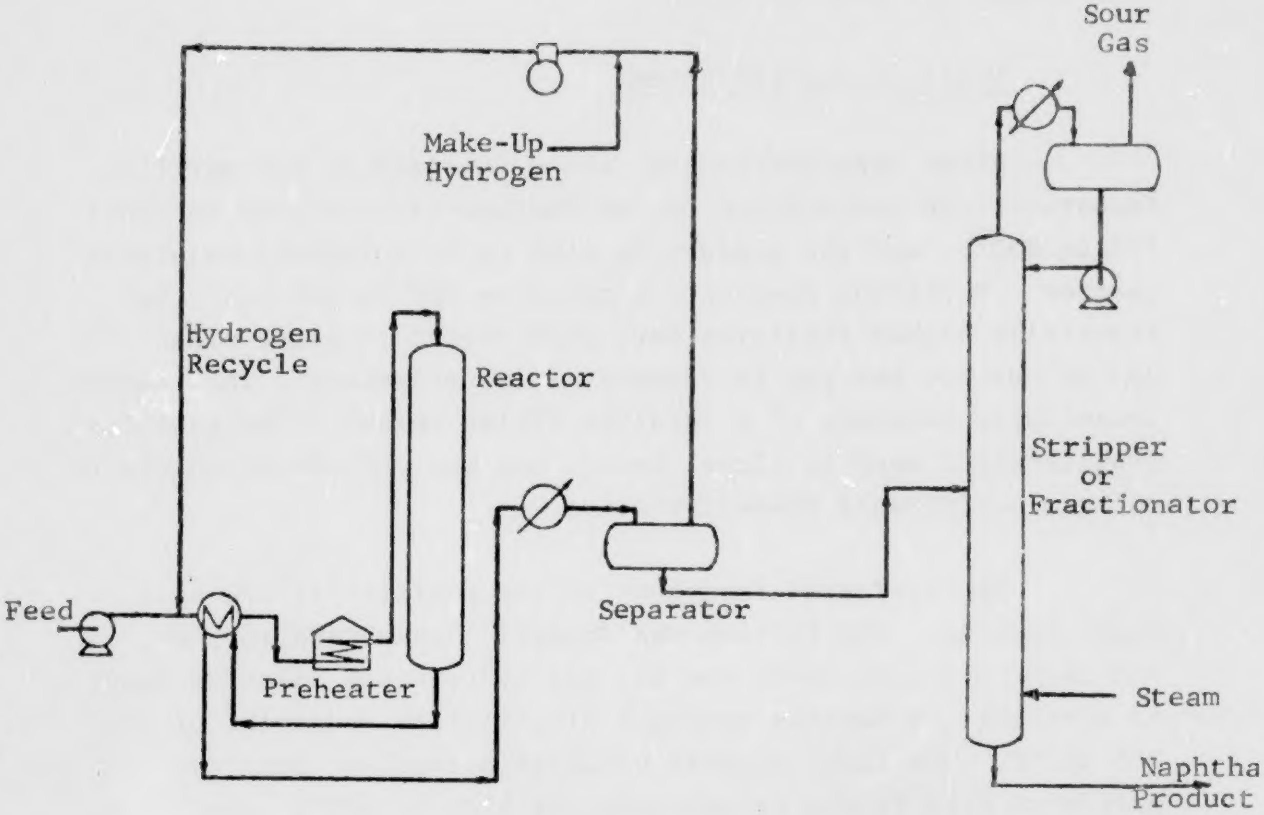

Sour Gas
Make-Up Hydrogen
Hydrogen Recycle
Reactor
Stripper or Fractionator
Separator
Feed
Preheater
Steam
Naphtha Product

FIGURE 2.3-2 NAPHTHA HYDRODESULFURIZATION UNIT

Once the H_2S has been removed from the naphtha stream, the sour gas may be flared, burned in a preheater or boiler, or routed to an amine treating unit. A choice between these alternatives is based on the economics and local air pollution regulations for each SNG plant.

Catalytic Gasification

After desulfurization, steam is added to the purified feedstock, the temperature of the mixture is increased to about 750 to 850°F, and the mixture is sent to an adiabatic catalytic reactor. Operating pressures range from 200 to 600 psi. Substantially higher pressures have been tested in pilot-plant operations but not yet in commercial installations. The reactor essentially consists of a catalyst filled vessel. The gasification catalyst used is nickel based, but may contain promoters to enhance performance characteristics.

The preferred feedstock to the gasifier is LPG or a light naphtha. The British Gas Council, Japan Gasoline Co., and BASF/Lurgi processes can all use hydrocarbon feeds as heavy as straight-run naphtha having a distillation end-point of about 356-365°F. The Lurgi process utilizes a catalyst that can gasify naphtha having an end-point as high as 400°F. Naphthas with higher end-points have been tested successfully in pilot-plant work, and it has been recently reported that the British Gas Council CRG process can handle naphtha feedstocks with a final boiling point up to 465°F (BE-246). However, catalyst life generally decreases as the average molecular weight and aromatic content increase. In addition, olefins tend to crack and form carbon on the catalyst, so only limited heavy materials amounts can be tolerated in the feedstock.

One feature of the Japan Gasoline Co. process is a catalyst that tolerates feed containing up to 3 ppm sulfur. It is reported that this catalyst is promoted with copper and chromium oxides (BR-103).

A portion of the gasified effluent from the catalytic gasifier can be recycled back to the entrance of the gasifier. This recycle is particularly desirable when gasifying heavy naphtha, but less advantageous when feeding light naphtha.

Range of composition for the gas leaving the reactor is typically as follows:

Component	Analyses (dry) Volume %
CH_4	60-75
CO_2	20-22
CO	0.5-1.0
H_2	10-18

An average Btu content for this stream in the CRG process is 680 Btu/scf (HY-014). The component analysis and Btu content of this stream is a function of the type process used as well as the operating conditions of the unit.

Methanation

Methanation is essentially a continuation of the gasification stage, but it occurs at a lower temperature to promote formation of methane. In some designs, the same catalyst may be employed for methanation as for gasification, or the catalyst may have the same basic composition but with different promoters.

One or two stages of methanation may be used, although it is more common to use two stages when gasifying naphtha. The number of stages, the operating temperature, and amount of steam left in the reacting gas are dependent on the product-gas specification (carbon monoxide and hydrogen contents, as well as heating value) and catalyst performance (i.e., ability to promote methanation in the presence of significant quantities of steam, and ability to avoid carbon formation in the presence of minuimum quantities of steam).

One process alternative possible in the methanation step, particularly when treating a light naphtha, is to intorduce part of the naphtha feed directly from the vaporizer into the first-stage methanator (which is the hydrogasification step in the British Gas Council process). This reduces total energy requirements but may increase catalyst investment costs and makeup requirements. The optimum design appears to be largely a function of naphtha composition.

The methanation step uses adiabatic catalyst beds. Representative temperatures may be 625-725°F in the first bed and 570-620°F in the second. A representative flow diagram for the gasification of naphtha using two methanators is shown in Figure 2.3-3.

Purification

The gas exiting from the methanation section contains significant amounts of carbon dioxide and some water vapor. Both of these components of the gas stream must be removed. The CO_2 must be taken out for improvement of the product-gas quality and heating value, and the H_2O removed to prevent condensation and corrosion in the transmission system. A typical analysis (dry basis) of the gas exiting from the final methanator is (HY-014):

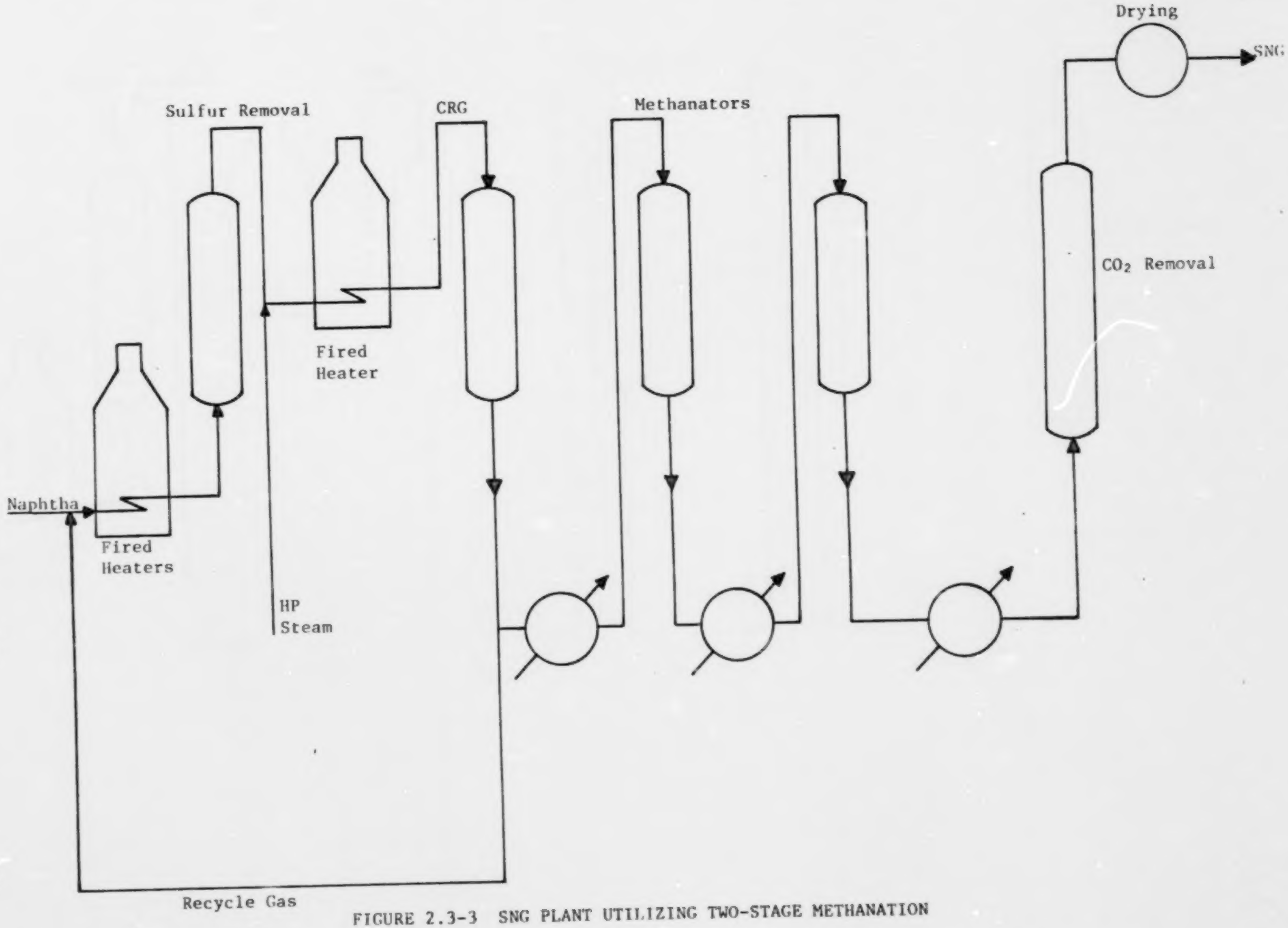

Drying
SNG
Sulfur Removal
CRG
Methanators
CO_2 Removal
Fired Heater
Naphtha
Fired Heaters
HP Steam
Recycle Gas

FIGURE 2.3-3 SNG PLANT UTILIZING TWO-STAGE METHANATION

CH_4	79.0 mole %
H_2	1.1 mole %
CO	< 0.1 mole %
CO_2	19.9 mole %

Any conventional CO_2- removal system may be used to improve product gas quality. Various activated hot carbonate processes, or other proprietary designs may be employed. Some of the more popular CO_2- removal systems are: Benfield, Diglycolamine or Econamine, Fluor Solvent, Girbitol, Selexol, Catacarb, and Sulfinol. A flow diagram of the Benfield process is shown in Figure 2.3-4.

The Benfield process pictured is similar in many respects to the other popular CO_2 removal methods mentioned. The raw gas is contacted with potassium carbonate solution containing Benfield additives in an absorber column. The CO_2 is absorbed here under pressures which range from 100 to 2000 psig in different units. The rich solution from the absorber is let down to about atmospheric pressure and stripped in a regenerator tower to drive off the absorbed CO_2. The regenerated solution is then recycled to the absorber and the CO_2 is vented to the atmosphere. A small amount of methane is lost through this CO_2 vent. The methane loss is estimated at about .074 lbs per 1000 scf of SNG produced (LO-095).

After CO_2 removal, the final step in the manufacture of SNG consists of gas dehydration. Numerous processes are available for the drying of the gas to meet pipeline specifications. Basically, the two alternatives are the dry-bed systems and the wet-scrubber systems. Either type can adequately dehydrate the SNG. The water which is recovered can be used as boiler make-up feed water or it can be used in the plant cooling water system.

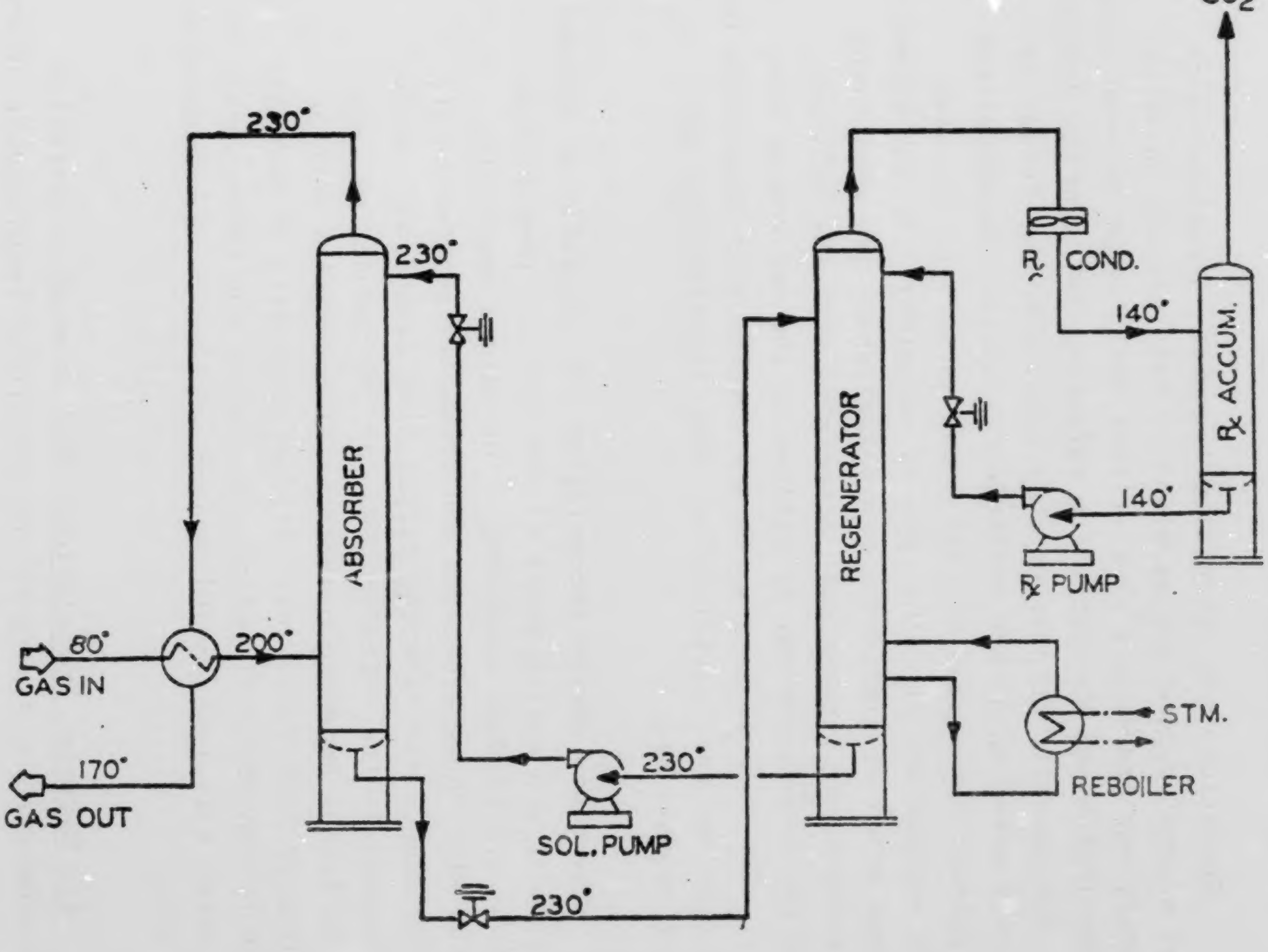

CO_2
230°
230°
ABSORBER
80°
GAS IN
200°
170°
GAS OUT
SOL. PUMP
230°
230°
REGENERATOR
R. COND.
140°
R. ACCUM.
140°
R PUMP
STM.
REBOILER

FIGURE 2.3-4 BENFIELD CO_2 REMOVAL UNIT

SOURCE: (IN-029)

2.4 New Technologies

Operations and processing sequences associated with advanced energy systems are examined in this section in order to identify any processing similarities which exist between these new technologies and the petroleum refining, SNG, and LNG industries. The specific purpose of this new technology survey is to identify areas which are sufficiently similar to operations in the subject industries of this study as to have the same emission sources and the same type of emissions. To the extent that these areas of similarity are established, the monitoring and emission control techniques associated with the refinery, SNG, and LNG industries may be related to the new energy technologies. The technologies which are specifically considered in this section are coal gasification, coal liquefaction, and shale oil production.

These new energy technologies may basically be divided into the major processing steps of raw material preparation, conversion, and product upgrading. The unique operations associated with these processes are primarily located in the conversion step. Raw material preparation techniques, while not duplicated in the refining, SNG, or LNG industries, are similar to solids handling operations in industries such as coal mining or rock quarrying. Product upgrading is normally performed by conventional refining processes and consequently is an area where emissions should be very similar to the industries in this study.

Raw Material Preparation: Raw material preparation involves crushing and sizing to the particular requirements of the conversion process being employed. In general, conventional preparation and solids handling techniques are used. The operations in this processing step do not resemble any procedures used in the refining, SNG, or LNG industries; however, the preparation techniques are similar to operations in established industries such as coal mining. Potential emissions and emission sources which may result from this processing step include the following:

- particulates from crushing and sizing operations
- particulates and combustion products from thermal dryers
- combustion products from internal combustion sources
- fugitive particulate emissions from solids handling, transportation, and ore stockpiles
- ore stockpile run-off (weathering of organics, leaching of water-soluble components)
- solid wastes from crushing and sizing operations
- solids and/or water from particulate control systems.

Conversion: The converions step is normally the unique part of the process — the operation which not only distinguishes the process from existing industries but also characterizes the process within the specific energy technology. This step is the heart of the process and, as a result, impacts the amount of ore preparation and product upgrading required.

The new technological developments associated with the new energy systems are primarily related to this processing step. The conversion step is not similar to any operations in the refinery, SNG, or LNG industries. Conventional emission control techniques may, however, be applied to the extent that common emission sources resulting in fuel combustion and fugitive emissions exist within this processing step.

Product Upgrading: All new energy technologies require product upgrading since a marketable product is not produced directly from the conversion step. In general this processing step consists of product separation, gas recovery and purification, liquid product upgrading, and by-product recovery. This processing step utilizes conventional upgrading procedures and consequently involves many operations which are similar or identical to petroleum refining, SNG, or LNG processes. Processes which may be involved in this upgrading step are as follows:

distillation
gas treating
sulfur recovery
hydrotreating or hydrocracking
thermal cracking or coking
ammonia separation
shift conversion
methanation

Emission sources in this step include fuel combustion emissions from the various process heaters, sulfur compound emissions (SO_x, COS, CS_2) from the sulfur recovery unit, fugitive hydrocarbon emissions, ammonia emissions from ammonia handling facilities and hydrocarbon emissions from liquid product storage. Due to the metallic components in the coal and shale feed, trace metallic emissions may also potentially result from these processes. Although some metals are primarily retained in the ash and others may be detected in condensate streams (AT-042, FO-026) little work has been published to date concerning the specific fate of metallic components in the process streams.

In addition to the operations related to the three major processing steps, the new energy technologies utilize auxiliary processes such as power generation and water treating facilities. The auxiliary processes employ existing technology and represent another area where similarities exist between new energy systems and the industries of this study.

Therefore, the areas of new energy technologies which are similar to the refinery, SNG, or LNG industries, include the product upgrading processes and the auxiliary operations. Information presented in this study for the established industries should be applicable to these areas of the advanced energy systems. All of those areas of similarity represent air emission sources. Assuming that all solid wastes are combined into one waste stream, the impact of the coal ash or spent shale precludes any similarities with waste from the refinery, SNG, or LNG industries. Likewise the trace elements and trace organics associated with the coal or shale make the water treating problems involved with new energy technologies much more complex than processes utilizing an oil or gas feed. Although certain aspects of water treating such as pH, temperature, and suspended solids may be handled by conventional techniques, the overall water management problem associated with new energy technologies is not comparable to refinery, SNG, or LNG systems.

Despite the processing differences that occur in the new energy systems, many of the emissions are still the same as those encountered in established industries. Consequently, such emissions as the criteria air pollutants (particulates, SO_x, NO_x, CO, HC) will at least initially be controlled in the same manner as discussed in this report. The more pressing environmental problems associated with the new energy systems involve the distribution and form of trace elements and trace organics, water management (make-up and discharge), and solids handling and disposal.

2.4.1 Coal Gasification

Coal gasification involves the production of fuel gas by the reaction of the carbon in the coal with steam and oxygen. The processes of this energy technology may be divided into two groups depending upon the heating value of the product gas. Low Btu gasification processes produce a CO and H_2 rich gas which may have a heating value between 150-450 Btu/scf. High Btu gasification processes utilize more extensive upgrading operations to produce a pipeline quality gas of approximately 1000 Btu/scf.

Low Btu Gasification

The following processes are typically involved in a low Btu gasification system:

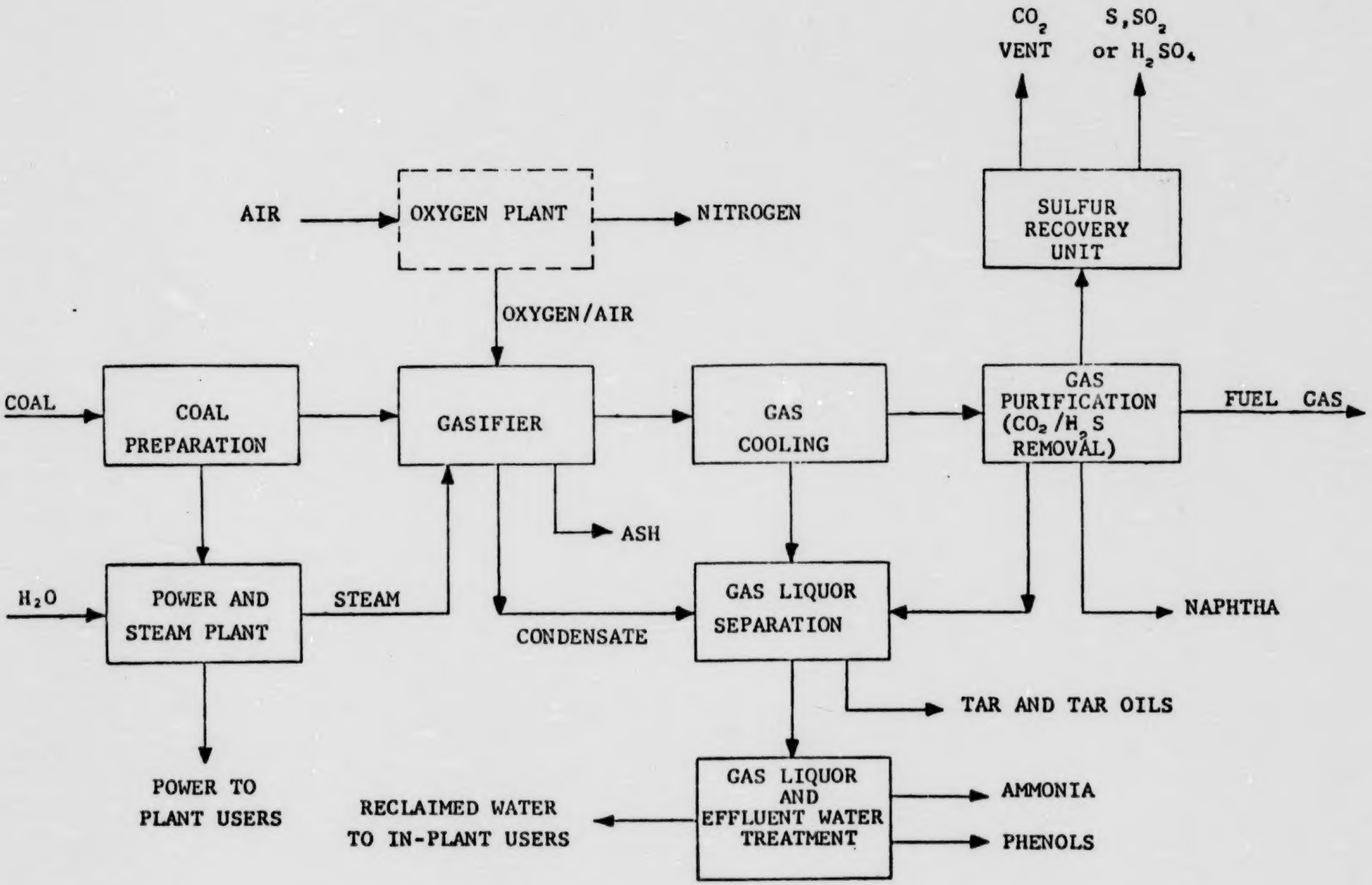
- coal preparation
- oxygen plant (optional)
- power and steam generation plant
- gasifier
- gas cooling
- gas liquor separation
- gas liquor and effluent water treatment (ammonia separation)
- gas purification
- sulfur recovery
- cooling water system

The processing sequence is illustrated in Figure 2.4-1. The oxygen plant is optional. If air is used as the oxygen source a low Btu gas (150-300 Btu/scf) is produced, whereas, if pure oxygen is fed to the gasifier, a medium Btu gas (300-450 Btu/scf) results.

Emission sources associated with low Btu gasification are as follows:

- Air emissions result from coal preparation, gasifier vents, process heaters, steam and power generation, sulfur recovery, fugitive particulate and hydrocarbon emission sources, ammonia storage, and hydrocarbon storage.
- Water effluents are projected to be controlled for zero discharge (US-112, US-164). Streams which may potentially contribute to a wastewater stream are coal pile run-off ash quench water, process wastewater, cooling tower blowdown, gas purification blowdown, and any water used in emission control systems.
- Solid waste is generated as discard from coal preparation, ash from gasifier, suspended solids in the make-up water, particulates from control systems, spent catalyst (periodic), and miscellaneous solids generated during cleaning and maintenance.

The gasifier is the unique part of this technology. The type of gasifier used characterizes the specific process. Although certain gasification procedures may in special situations be used in refineries, the gasification step is not



CO₂ VENT
S, SO₂ or H₂SO₄
AIR
OXYGEN PLANT
NITROGEN
SULFUR RECOVERY UNIT
OXYGEN/AIR
COAL
COAL PREPARATION
GASIFIER
GAS COOLING
GAS PURIFICATION (CO₂/H₂S REMOVAL)
FUEL GAS
ASH
H₂O
POWER AND STEAM PLANT
STEAM
CONDENSATE
GAS LIQUOR SEPARATION
NAPHTHA
TAR AND TAR OILS
POWER TO PLANT USERS
RECLAIMED WATER TO IN-PLANT USERS
GAS LIQUOR AND EFFLUENT WATER TREATMENT
AMMONIA
PHENOLS

FIGURE 2.4-1 LOW BTU GASIFICATION PROCESS

considered to be similar to the normal processing operations of the industries of this study.

Areas such as coal preparation and oxygen generation utilize conventional technology, but the refining, SNG, and LNG industries do not normally utilize similar processes. Effluent water treatment and ammonia separation operations may also utilize existing technology; however, ammonia production is not always economically feasible in petroleum refining and water treating should not be considered similar due to the potential impact of trace elements in the coal. Processes which are similar to operations of industries in this study include power and steam generation, gas cooling, gas liquor separation, gas purification, sulfur recovery, and cooling water systems. Therefore, emission sources which are similar to the refining, SNG, or LNG industries are:

- fuel combustion emissions from power and steam generation
- sulfur compound emissions from sulfur recovery (SO_x, COS, CS_2)
- fugitive hydrocarbon sources
- hydrocarbon emissions from liquid by-products storage

High Btu Gasification

High Btu gasification processes produce essentially pure methane from the coal by adding hydrogen derived from steam and discarding carbon in the form of CO_2 and/or char. The main difference from low Btu processing is the inclusion of shift conversion and methanation processes in the processing sequence. The processing sequence for a typical high Btu gasification process is shown in Figure 2.4-2. Emission sources are the same as for low Btu gasification with the addition of the following sources:

- fuel combustion emissions from process heaters associated with shift conversion and methanation
- fugitive emission sources associated with shift conversion, methanation, and compression
- water effluent from dehydration of pipeline gas.

The same processing similarities also exist between high Btu processes and the refining, SNG and LNG industries.

Emission sources which are similar to these industries are

- fuel combustion emissions from process heaters
- fuel combustion emissions from power and steam generation
- SO_x emissions from sulfur recovery
- fugitive hydrocarbon sources
- hydrocarbon emissions from liquid by-products storage.

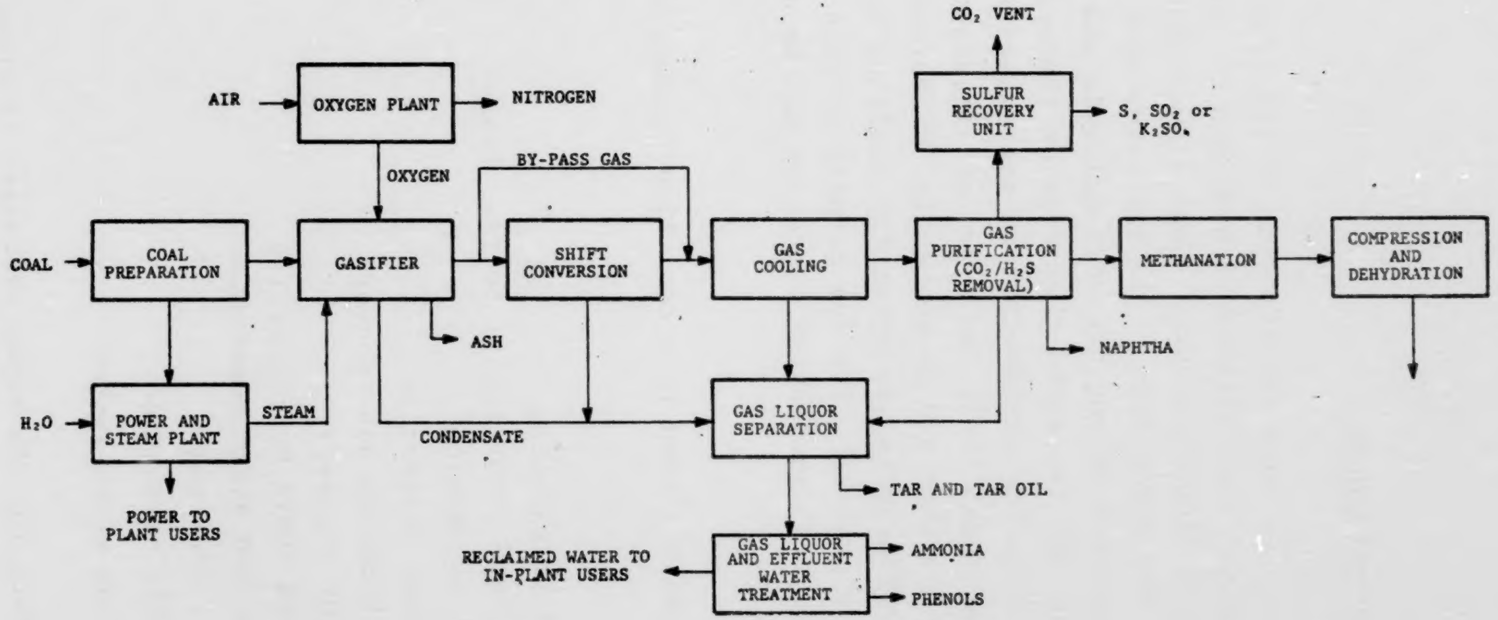

AIR
OXYGEN PLANT
NITROGEN
OXYGEN
COAL
COAL PREPARATION
GASIFIER
BY-PASS GAS
SHIFT CONVERSION
GAS COOLING
CO₂ VENT
SULFUR RECOVERY UNIT
S, SO₂ or K₂SO₄
GAS PURIFICATION (CO₂/H₂S REMOVAL)
METHANATION
COMPRESSION AND DEHYDRATION
ASH
NAPHTHA
H₂O
POWER AND STEAM PLANT
STEAM
CONDENSATE
GAS LIQUOR SEPARATION
TAR AND TAR OIL
POWER TO PLANT USERS
RECLAIMED WATER TO IN-PLANT USERS
GAS LIQUOR AND EFFLUENT WATER TREATMENT
AMMONIA
PHENOLS

FIGURE 2.4-2 HIGH BTU GASIFICATION PROCESS

2.4.2 Coal Liquefaction

The basis of coal liquefaction is the cracking of the coal molecule and the addition of hydrogen or removal of carbon to produce a liquid product. Coal liquefaction processes fall into one of two categories - (1) processes that utilize hydrogen to assist in cracking the coal molecule and increasing the H:C ratio, and (2) processes that rely on thermal cracking and the removal of carbon (carbonization processes) to increase the H:C ratio. Although these two types of liquefaction processes have different approaches and consequently, different technical problems, these differences are primarily confined to the reactor section of the process. For the purpose of this analysis the two categories of liquefaction processes may be considered at the same time.

Processes utilized in a coal liquefaction plant are as follows:

- coal preparation
- hydrogen production (gasifier train)
- coal conversion
- product separation
- gas treating and recovery
- sulfur recovery
- liquid fuels hydrotreating
- power and steam generation
- water treating
- ammonia separation
- cooling water systems

A processing sequence for the major processes is shown in Figure 2.4-3. If a gasifier is employed for char utilization and hydrogen production the operations associated with low Btu gasification (Figure 2.4-1) may be included as part of the gasifier train. Depending upon the complexity of the liquefaction

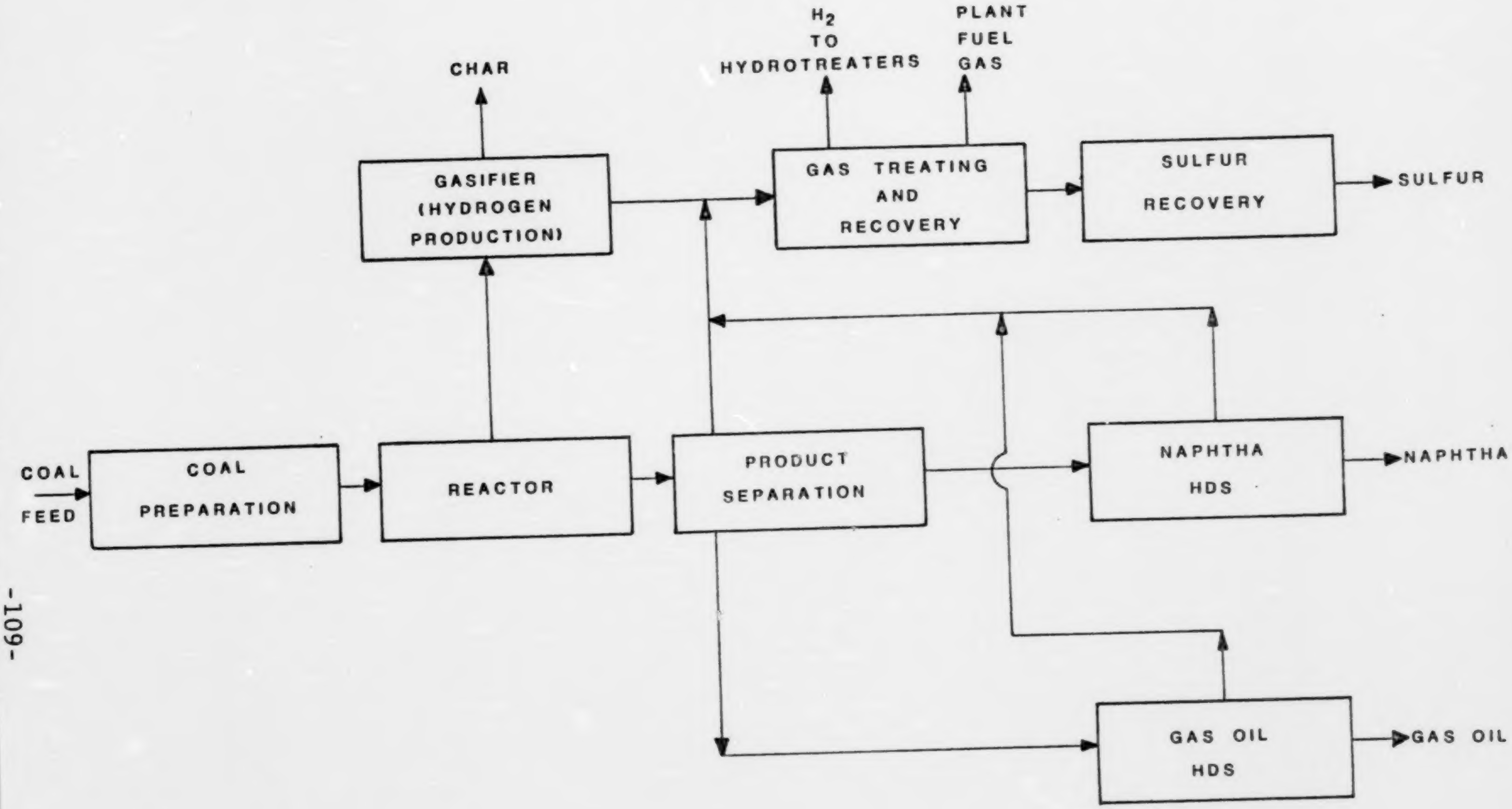

CHAR
H_2 TO HYDROTREATERS
PLANT FUEL GAS
GASIFIER (HYDROGEN PRODUCTION)
GAS TREATING AND RECOVERY
SULFUR RECOVERY
SULFUR
COAL FEED
COAL PREPARATION
REACTOR
PRODUCT SEPARATION
NAPHTHA HDS
NAPHTHA
GAS OIL HDS
GAS OIL

FIGURE 2.4-3 COAL LIQUEFACTION PROCESS

plant and the flexibility desired, a shift converter and methanation may also be included in the gas processing sequence.

Emission sources associated with coal liquefaction are as follows:

- Air emissions result from coal preparation, process heaters, steam and power generation, sulfur recovery, fugitive particulate and hydrocarbon emission sources, ammonia storage, and hydrocarbon storage.

- Water blowdown and waste streams are expected to be sufficiently minimized to allow containment in evaporation ponds and, therefore, result in a zero water discharge (BA-230, HI-083). Streams which may potentially contribute to a wastewater stream are coal pile run-off, ash quench water, process wastewater, cooling tower blowdown, gas treating blowdown, and any water used in emission control systems.

- Solid waste is generated as discard from coal preparation, ash from gasifier, suspended solids in the make-up water, particulates from control systems, spent catalyst (periodic), and miscellaneous solids generated during cleaning and maintenance.

Coal liquefaction processing areas which are not similar to the industries of this study are coal preparation, coal conversion, and char gasification (hydrogen production). Although conventional water treating techniques may be used, water treating cannot be considered an area of similarity due to the potential for trace elements and trace organics from the coal. The ammonia separation is accomplished with conventional techniques; however, this by-product recovery operation is essentially an optional process which may not be economically attractive in many refining operations. Processes which may definitely be considered to have corresponding operations in the refinery, SNG, or LNG industries include product separation, gas treating and recovery, sulfur recovery, liquid fuels hydrotreating, power generation, and cooling water systems. The emission sources which these processes represent are the common sources between the new energy systems and the industries of this study. These sources are as follows:

- fuel combustion emissions from process heaters
- fuel combustion emissions from power plants
- sulfur compound emissions from the sulfur recovery stack (SO_x, COS, CS_2)
- fugitive hydrocarbon emissions
- hydrocarbon emissions from storage

2.4.3 Shale Oil Production

Oil shale is a naturally occurring deposit consisting of a mixture of several minerals and kerogen, a solid organic constituent which may be converted to conventional petroleum products. A typical oil shale contains approximately 12 wt % kerogen or about 30 gallons of oil per ton. In order to decompose the kerogen and obtain the hydrocarbon products, the shale must be heated to approximately 900°F. This heating (retorting) step is the base requirement of all oil shale processes. Oil shale processes may be divided into two major classes, depending upon whether the retorting occurs above or below ground (ex situ or in situ).

In situ processing involves fracturing the shale, injection of retorting fluids, retorting of the shale in-place, recovery of the product, and shale oil upgrading processes. The intriguing advantage of in situ processing is that the massive solids handling and disposal problems associated with ex situ processes may be avoided. In situ oil shale processing is, however, still in the conceptual stage, whereas ex situ processing, which relies on more developed technology, is much more advanced. Since the shale oil upgrading procedures are essentially the same for both in situ and ex situ processes, the comparison of similarities between oil shale processing and the refining, SNG, and LNG is made by examining ex situ processes.

Processes involved with ex situ shale oil processing are as follows:

- raw shale preparation
- retorting
- spent shale moisturizing and disposal
- product separation
- gas treating and recovery
- sulfur recovery
- hydrogen production
- delayed coking
- liquid product hydrotreating
- power generation
- water treating
- ammonia separation
- cooling water systems

A processing sequence for the major processes is shown in Figure 2.4-4.

Emission sources associated with shale oil production are as follows:

- Air emissions result from raw shale preparation, retort preheaters, spent shale moisturizers, spent shale handling, process heaters, steam and power generation, sulfur recovery, fugitive particulate and hydrocarbon emission sources, ammonia storage, and hydrocarbon storage.
- Water effluents are projected to be controlled for zero discharge (US-093, CO-175). Streams which may potentially contribute to a wastewater stream are raw shale pile run-off, process wastewater, cooling tower blowdown, gas purification blowdown, spent shale disposal run-off, and any water from emission control systems.
- Solid waste is generated as discard from raw shale preparation, spent shale, suspended solids in the make-up water, particulates from control systems, spent catalyst (periodic), and miscellaneous solids generated in cleaning and maintenance.

Areas of shale oil production which are not similar to the industries of this study are raw shale preparation, retorting, and spent shale moisturizing and disposal. Effluent water treatment and ammonia separation operations may utilize

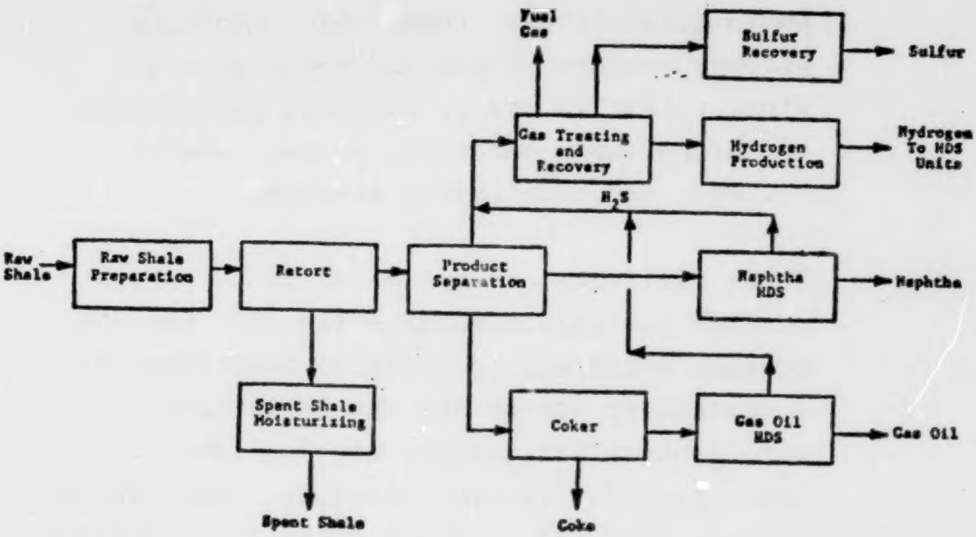

Raw Shale
Raw Shale Preparation
Retort
Product Separation
Spent Shale Moisturizing
Spent Shale
Fuel Gas
Gas Treating and Recovery
Sulfur Recovery
Sulfur
Hydrogen Production
Hydrogen To HDS Units
H_2S
Naphtha HDS
Naphtha
Coker
Coke
Gas Oil HDS
Gas Oil

FIGURE 2.4-4 SHALE OIL PROCESS

existing technology; however, ammonia production is not always economically feasible in refining operations and water treating should not be considered similar due to the potential impact of trace elements in the shale. Processes which are similar to industries of this study are product separation, gas treating and recovery, sulfur recovery, hydrogen production, delayed coking, liquid product hydrotreating, and power generation and cooling water systems. Emission sources which are similar to the refinery, SNG, or LNG industries are:

- fuel combustion emissions from process heaters
- fuel combustion emissions from power generation
- sulfur compound emissions from sulfur recovery (SO_x, COS, CS_2)
- fugitive hydrocarbon emissions
- hydrocarbon emissions from liquid product storage.

3.0 IDENTIFICATION OF EMISSIONS AND EFFLUENTS

Utilizing the typical industry processing sequences developed in Section 2.0, representative process modules for the following are presented in this section:

- fuel oil refinery
- gasoline refinery
- SNG plant
- LNG plant

There are many processing alternatives possible in petroleum refinery operations; however this discussion is limited to two refinery modules. While fuel oil and gasoline production represent two different areas of processing, together they account for the bulk of refinery output. In addition these two types are representative of a large number of existing refineries as well as major demand areas for new refinery applications.

Module flow rates are determined assuming typical size commercial plant operation and utilizing specific process yield data. After each module is established in terms of processes, flow rates, and energy or fuel demand, the emission sources and emissions are presented. Emissions are related to specific sources and organized according to the media impacted (air emission, water effluent, and solid waste). Only criteria pollutants such as particulates, SO_x, CO, NO_x, and HC are quantified. The water pollutants which are quantified include BOD, COD, ammonia sulfides, total phosphorous, phenol, oil, suspended solids, and dissolved solids. The solid wastes are just considered as the total weight of solids produced.

All of the emissions are related to the module basis, allowing for convenient assessment of a typical plant impact. Emissions from all modules are also adjusted to a common Btu output basis for comparison of emission impacts among the various technologies.

3.1 Fuel Oil Refinery Module

3.1.1 Module Basis

The fuel oil refinery module is based on a typical commercial size operation of 200,000 barrels per day crude capacity.* The emission values calculated in the fuel oil refinery section are, therefore, presented on this 200,000 BPD basis. A summary of total calculated emissions from the fuel oil refinery module is shown in Table 3.1-1.

3.1.2 Module Description

The crude feedstock for this module is assumed to have a 31°API gravity and a sulfur content of 1.5 wt%. The heating value of the crude is assumed to be 5.8×10^6 Btu/bbl (BA-230). Characteristics of the crude charge are summarized in Table 3.1-2.

The processing sequences utilized in this module are shown in Figure 3.1-1 along with the major process flow rates. The liquid product yield resulting from this module per barrel of crude is as follows:

· motor gasoline	0.43 bbl
· light fuel oil	0.42 bbl
· heavy fuel oil	0.08 bbl

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*All flow rates for this module are based on calendar days.

TABLE 3.1-1

SUMMARY OF ENVIRONMENTAL IMPACT

Fuel Oil Refinery Module

Basis: 200,000 bbl/day Crude Feed

Air (lb/day)	
Particulates	6,320
SO_x	16,000
NO_x	11,830
CO	1,200
Hydrocarbons	73,970
Water (lb/day)	
Suspended Solids	250
Dissolved Solids	9,260
Organic Material	52.5
Solid Wastes (tons/day)	4.0

TABLE 3.1-2

CRUDE FEEDSTOCK CHARACTERISTICS

Fuel Oil Refinery Module

Crude Characteristics	
API° Gravity	31
Sulfur Content	1.5 wt%
Heating Value	5.8x10^6 Btu/bbl

True Boiling Point Range	Wt% of Crude
68/375 °F	20.4
375/600 °F	19.1
600/1050 °F	36.0
1050+ °F	24.5

FUEL OIL REFINERY MODULE

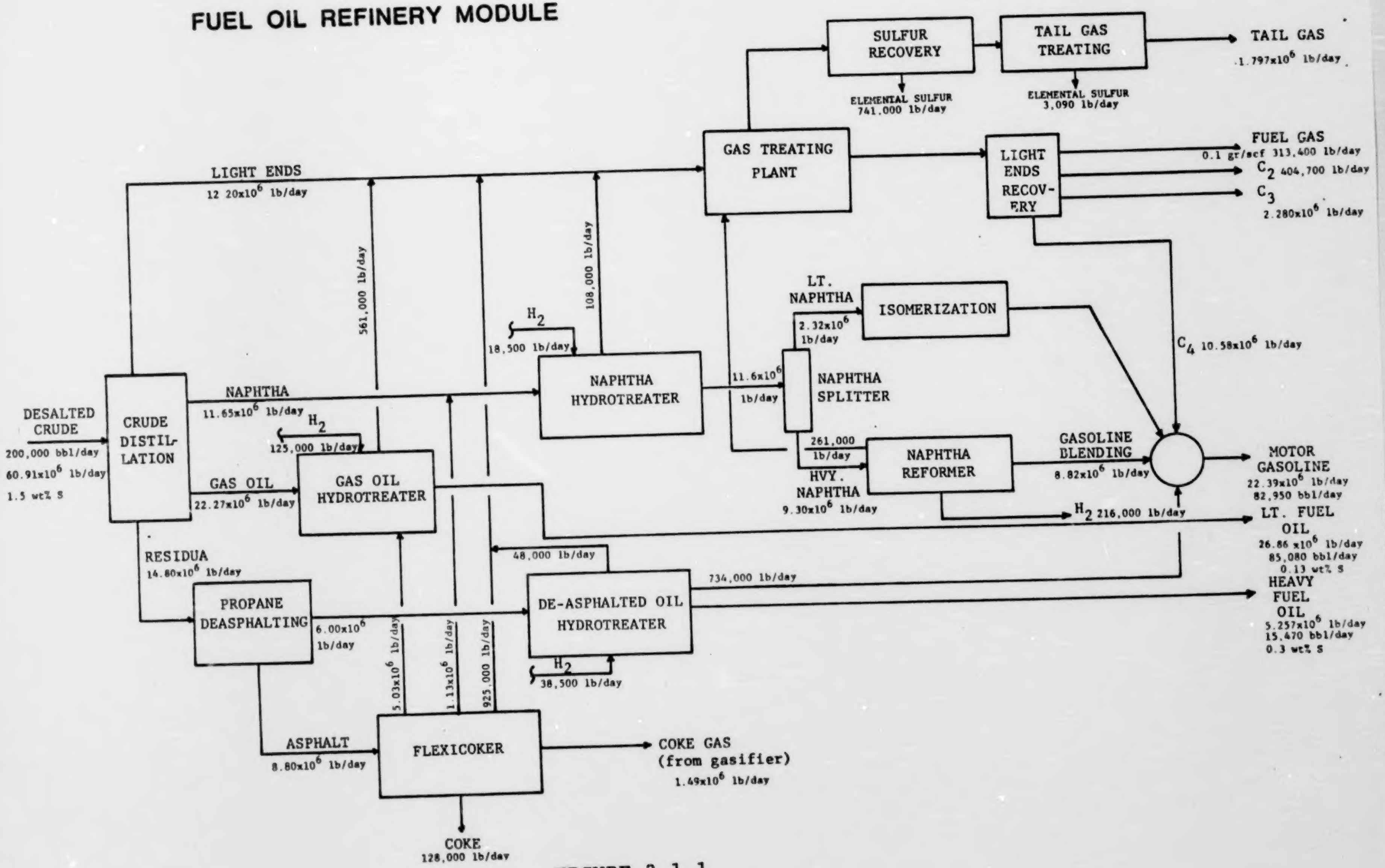

DESALTED CRUDE
200,000 bbl/day
60.91x10⁶ lb/day
1.5 wt% S
CRUDE DISTIL-LATION
LIGHT ENDS
12 20x10⁶ lb/day
NAPHTHA
11.65x10⁶ lb/day
GAS OIL
22.27x10⁶ lb/day
RESIDUA
14.80x10⁶ lb/day
H2
125,000 lb/day
GAS OIL HYDROTREATER
561,000 lb/day
H2
18,500 lb/day
NAPHTHA HYDROTREATER
108,000 lb/day
11.6x10⁶ lb/day
NAPHTHA SPLITTER
LT. NAPHTHA
2.32x10⁶ lb/day
ISOMERIZATION
261,000 lb/day
HVY. NAPHTHA
9.30x10⁶ lb/day
NAPHTHA REFORMER
GASOLINE BLENDING
8.82x10⁶ lb/day
H2 216,000 lb/day
GAS TREATING PLANT
SULFUR RECOVERY
ELEMENTAL SULFUR
741,000 lb/day
TAIL GAS TREATING
ELEMENTAL SULFUR
3,090 lb/day
TAIL GAS
1.797x10⁶ lb/day
LIGHT ENDS RECOV-ERY
FUEL GAS
0.1 gr/scf 313,400 lb/day
C2 404,700 lb/day
C3
2.280x10⁶ lb/day
C4 10.58x10⁶ lb/day
MOTOR GASOLINE
22.39x10⁶ lb/day
82,950 bbl/day
LT. FUEL OIL
26.86 x10⁶ lb/day
85,080 bbl/day
0.13 wt% S
HEAVY FUEL OIL
5.257x10⁶ lb/day
15,470 bbl/day
0.3 wt% S
PROPANE DEASPHALTING
6.00x10⁶ lb/day
48,000 lb/day
DE-ASPHALTED OIL HYDROTREATER
734,000 lb/day
H2
38,500 lb/day
5.03x10⁶ lb/day
1.13x10⁶ lb/day
925,000 lb/day
ASPHALT
8.80x10⁶ lb/day
FLEXICOKER
COKE GAS
(from gasifier)
1.49x10⁶ lb/day
COKE
128,000 lb/day

FIGURE 3.1-1

The crude feed to the refinery is first desalted and then routed to a crude distillation unit where the crude is distilled both at atmospheric pressure and in a vacuum column to produce four product cuts: (1) sour light ends (C_1-C_4 hydrocarbons), (2) naphtha, (3) gas oil, and (4) vacuum resid. The resid product is routed to a propane deasphalting unit for extraction of gas oil. The deasphalted oil from this unit is then hydrotreated for sulfur removal. The three product streams resulting from hydrotreating are sour light ends, naphtha, and heavy fuel oil. The heavy fuel oil is recovered and either routed to product tankage or used to fire process heaters within the refinery. The naphtha stream is routed to the gasoline blending area. The light ends formed are routed to the gas treating plant for acid gas removal.

The asphalt produced at the propane deasphalting unit is fed to a flexicoker. The flexicoker acts as a fluid bed coking unit and a coke gasifier. The fluid bed section produces a sour naphtha stream and a sour light ends stream. The gasifier produces the final coke product and a low Btu coke gas which is sweetened and fired in the propane deasphalting unit process heater. The light ends from the flexicoker go the the gas treating plant. The naphtha product is combined with the straight run naphtha cut from the crude distillation unit and routed to a naphtha hydrotreater.

The crude naphtha and naphtha from the flexicoker are hydrotreated for removal of sulfur. The sour light ends produced go to the gas treating plant. The sweetened naphtha is split into a light naphtha stream (True Boiling Point 68-180°F) and a heavy naphtha stream (True Boiling Point 180-375°F). This split is defined, assuming that the incoming stream is 20 wt percent light naphtha and 80 wt percent heavy naphtha. The light naphtha from the hydrotreater is fed to a C_5/C_6 isomerization unit. The isomerization unit is used to increase the octane rating of pentane and hexane fractions by catalytically rearranging normal paraffins into isoparaffins. The heavy naphtha from the hydrotreater is fed to a catalytic reformer. The catalytic reforming process converts low octane naphtha into high octane naphtha by catalytically rearranging and dehydrogenating naphthenes and paraffins, forming benzenes, toluenes, and xylenes. The products of these two naphtha streams are blended along with other petroleum components for motor gasoline.

All of the collected sour light ends are amine treated in the gas treating plant for removal of the H_2S. The sweetened light ends are then recovered as fuel gas, ethane (C_2), propane (C_3), and butane (C_4) products. The fuel gas is burned in process heaters, while the butanes are blended with the motor gasoline. The ethane and propane rich product streams are routed to pressurized storage vessels or product lines.

The acid gas from the gas treating plant goes to a sulfur recovery facility for hydrogen sulfide removal. A Claus plant in conjunction with a tail gas treating unit is utilized for sulfur recovery. In the Claus plant the H_2S is partially combusted with oxygen and stoichiometrically reacted to form a solid elemental sulfur product and water. Hydrogen sulfide removal ranges from 95 percent to 98 percent in this unit (HY-014). The tail gas from the Claus plant is routed to a Tail Gas Treating Unit for additional sulfur removal. After conversion of all sulfur species in the gas to H_2S, the tail gas is contacted with an alkanolamine solution for H_2S removal. This final tail gas treating unit results in a total equivalent sulfur removal from the acid gas stream of greater than 99.8 percent (HY-014).

The liquid wastes accumulated from the fuel oil refinery module are treated in both primary and secondary waste water treatment facilities. The secondary treating can be either activated sludge or aerated lagoons. The sludge from this treatment is incinerated. Auxiliary units such as waste water treating facilities and incinerators are not shown in Figure 3.1-1.

The module heat requirements are calculated utilizing the module flow rates and the specific process utility demand information. The total module heat demand is 4.47 x 10^{10} Btu per day. After specific module heat demands are established, the allocations of the refinery fuels to meet these demands are determined.

All of the fuel gas produced from the refinery module is allocated and consumed within the refinery. Fuel gas is preferentially used in the smaller process heaters. The fuel gas is capable of supply 7.47 x 10^9 Btu per day with a calculated heating value of about 900 Btu per scf. The remainder of the heat is essentially supplied by 0.3 wt percent sulfur fuel oil. The fuel oil has a heating value of 6.3 x 10^6 Btu per barrel (EN-071). Low Btu coke gas from the gasifier will supply a minor portion of the heat demand. The coke gas has a heating value of 1,598 Btu per pound and supplies 2.38 x 10^9 Btu per day (FL-047). The specific fuels used in each refinery module unit are shown in Table 3.1-3.

TABLE 3.1-3
FUEL OIL REFINERY
MODULE HEAT REQUIREMENTS

Unit	Unit Heat Requirement (Btu/day)	Fuel Used
Crude Unit	2.0×10^{10}	Fuel Oil
Gas Oil Hydrotreater	4.67×10^{9}	Fuel Oil & Fuel Gas
Naphtha Hydrotreater	1.01×10^{9}	Fuel Gas
Heavy Naphtha Reformer	1.272×10^{10}	Fuel Gas
Propane Deasphalting	3.65×10^{9}	Coke Gas & Fuel Gas
Deasphalted Oil Hydrotreater	1.57×10^{9}	Fuel Gas
C_5/C_6 Isomerization	7.78×10^{8}	Fuel Oil
Tail Gas Treating	1.80×10^{6}	Fuel Gas
Light Ends Recovery	1.40×10^{8}	Fuel Gas

3.1.3 Module Emissions

3.1.3.1 Air Emissions

Air emissions from the fuel oil refinery module result from fuel combustion, sulfur recovery, sludge incineration, petroleum storage, and miscellaneous hydrocarbon emissions throughout the refinery units. Module air emissions from the specific sources are given in Table 3.1-4.

Fuel Combustion Emissions

Utilizing fuel demand data for the various processes, fuel combustion emission sources are determined to be the following (HY-013, HY-014):

- crude distillation
- gas oil hydrotreater
- naphtha hydrotreater
- heavy naphtha reformer
- C_5/C_6 isomerization
- propane deasphalting unit
- deasphalted oil hydrotreater
- tail gas treating plant
- light ends recovery

Although each unit may contain several fuel combustion emission sources, all flue gas streams within one unit are assumed to be combined and routed to one stack. Therefore, each unit requiring fuel combustion represents one emission source. The emissions from each unit are based on the type of fuel used, such as fuel gas, fuel oil, or coke gas, and the EPA emission factors. These factors are shown in Table 3.1-5. The SO_x emissions from

TABLE 3.1-4

MODULE ATMOSPHERIC EMISSIONS

FUEL OIL REFINERY MODULE

(lb/day)

Basis: 200,000 bbl/day Crude Feed

	Particulates	SO_x	CO	Hydrocarbons	NO_x
Crude Distillation	3,080	6,400	533	533	5,330
Gas Oil Hydrotreater	280	539	90	128	1,084
Naphtha Hydrotreater	19	27	16.2	27.7	219
Hvy. Naphtha Reformer	1,960	4,073	340	340	3,390
Propane Deasphalting Unit	474	673	49.6	84.8	680
Deasphalted Oil Hydrotreater	30	42	25.2	42.9	340
Tail Gas Treating	3.4	3,410*	3.0	4.9	39
Light Ends Recovery	2.6	3.7	2.2	3.8	30.4
C_5/C_6 Isomerization	120	250	21	20.8	208
Storage					
1) Crude	-	-	-	7,550	-
2) Motor Gasoline	-	-	-	3,730	-
3) Light Fuel Oil	-	-	-	564	-
4) Heavy Fuel Oil	-	-	-	Neg	-
Sludge Incineration	354	597	125	41	510
Miscellaneous Emissions	-	-	-	60,900	-
TOTAL	6,320	16,000	1,200	73,970	11,830

* Mainly Due to the Tail Gas Itself

TABLE 3.1-5
EMISSION FACTORS FOR FUEL OIL
REFINERY FUEL USE

Air Pollutant	Fuel Gas lb/1000 SCF	Fuel Oil lb/barrel	Coke Gas† lb/1000 SCF
Particulates	0.02	0.97	0.02
Sulfur Oxides (SO_x)	2 x S_G*	6.72 x S_O**	2 x S_G*
CO	0.017	0.168	0.0013
Hydrocarbons	0.029	0.168	0.0022
Nitrogen Oxides (NO_x)	0.23	1.68	0.018

---

* S_G is Equal to the Sulfur Concentration of the Gas.

** S_O is Equal to the Weight Percent Sulfur in the Fuel Oil.

† Calculated Using EPA Emission Factors and the Ratio of Coke Gas to Fuel Gas Heating Values.

Source: (EN-071)

the fuel oil are calculated using a sulfur content of 0.3 wt percent. The SO_x emissions from combustion of fuel gas are calculated assuming the H_2S concentration in the fuel gas is in compliance with the Federal regulation of 0.10 grain per dscf (ST-124).

Due to the different composition of the coke gas, estimated values for the coke gas emission factors had to be determined. The particulates emission factor is assumed to be the same as the fuel gas. The SO_x emission factor is also assumed the same and based on a hydrogen sulfide concentration in compliance with the Federal standard of 0.10 grain/dscf (ST-124). The emission factors for CO, hydrocarbons, and nitrogen oxides are determined by multiplying the EPA fuel gas emission factors for each of these constituents by the ratio of the heating value of the coke gas to the heating value of the fuel gas.

Sulfur Recovery Emissions

The efficiency of sulfur removal by the sulfur recovery plant and the tail gas treating plant is approximately 99.8 percent (HY-014). The 0.2 percent not recovered is exhausted as SO_2 at a rate of 3,410 lb/day. The tail gas is routed to a stack within the refinery.

Sludge Incineration Emissions

The oily sludge from the API separator and the biological sludge from the waste treatment facilities are both incinerated. The quantity of oil incinerated in the oily sludge is based on the following (MA-226).

(1) 0.0015 bbl of oily sludge/bbl crude throughput is produced,

(2) Oily sludge is 36.6 wt percent oil, and

(3) Weight of the sludge is 340 lb/bbl.

The emissions from burning the oily sludge are based on the assumption that the oil in the sludge has the same characterisitcs of fuel oil and thus the same emissions factors (EN-071).

The biological sludge produced in the refinery is calculated to be 4280 lb/day. This value is based on the following:

(1) 9,000 lb BOD removed/day (US-056),

(2) 0.5 lb volatile solids formed/lb of BOD removed (BE-047), and

(3) The BOD removal efficiency is 95 percent (BE-047).

The emission factors used for biological sludge are the EPA emission factors for municipal wastes (EN-071). The emission factors are given in Table 3.1-6.

Petroleum Storage Emissions

In order to calculate the hydrocarbon emissions from petroleum storage, the following assumptions are used:

(1) Storage capacity is one month for both feed and products.

TABLE 3.1-6

SLUDGE INCINERATION EMISSION FACTORS

Pollutant	Oily Sludge lb Emission/1,000 gal Sludge	Biological Sludge lb Emission/Ton
Particulates	23	30
SO_2	47	2.5
CO	4	35
Hydrocarbons	3	1.5
NO_x	40	3

(2) Only crude, gasoline, and light fuel oil storage will result in hydrocarbon emissions.

(3) Heavy fuel oil storage and pressurized storage of high volatility products will result in negligible hydrocarbon emissions.

(4) Crude, gasoline, and fuel oils will be stored in floating roof tanks.

EPA emission factors for storage in floating roof tanks are used to calculate petroleum storage emissions. These factors are as follows (EN-071):

.	crude	-	0.029 lb/day-10^3 gal
.	gasoline	-	0.033 lb/day-10^3 gal
.	light fuel oil	-	0.0052 lb/day-10^3 gal

Miscellaneous Hydrocarbon Emissions

There are numerous miscellaneous hydrocarbon emissions in petroleum refineries which escape from sources such as valve stems, flanges, loading racks, equipment leaks, pump seals, sumps, drains, sewers, rupture discs, and API separators. Based on literature data, these miscellaneous hydrocarbon emissions amount to about 0.1 percent of the refinery capacity for a new, well-designed, well-maintained refinery (RA-119, DA-069, MS-001, AM-055). The composition of these hydrocarbons can be expected to be a composite of all volatile intermediate and refined products.

3.1.3.2 Water Effluents

Module water effluents have been estimated from published information (RA-119). The wastewater generation rate is taken as 15 gallons per barrel of crude feed. This value is believed to be reasonable considering modern water conservation techniques, segregation of wastewater streams, air cooling, and recycle. The concentrations of the pollutants are based on the efficiencies of primary and secondary wastewater treatment facilities. These concentrations are given in Table 3.1-7.

3.1.3.3 Solid Wastes

The solid wastes from a refinery are highly variable. Possible sources of solid waste in a refinery are the following:

(1) entrained solids in the crude,

(2) silt from surface drainage,

(3) silt from water supply,

(4) corrosion products from process units and sewer systems,

(5) solids from maintenance and cleaning operations,

(6) water treatment facilities, including ash from the sludge incinerator, and

(7) spent catalyst.

With the exception of spent catalyst, all the solids collect in the API separator and the waste water treating facilities. The

TABLE 3.1-7

WASTEWATER EFFLUENT QUALITY

Fuel Oil Refinery

Basis: 200,000 bbl/day Crude Feed

Flow Rate - 3.0×10^6 gal/day

	Concentration
BOD	15 ppm
COD	80 ppm
Ammonia	2 ppm
Hydrogen Sulfide	0.1 ppm
Total Phosphorous	2 ppm
Phenol	0.1 ppm
Oil	2 ppm
Suspended Solids	10 ppm
Dissolved Solids	370 ppm

Source: (RA-119)

solid waste is estimated at four tons per day. Three of the four tons per day are from the solid wastes from the API separator and the wastewater treatment facility. The other ton is from spent catalyst and is only an average of the intermittent catalyst regenerations. The solid wastes are suitable for landfill.

3.2 Gasoline Refinery Module

3.2.1 Module Basis

The gasoline refinery basis is the same as the basis used for the fuel oil refinery, a crude feed rate of 200,000 bbl/day.* The emissions given in this section for a gasoline refinery are presented on this 200,000 barrel feed basis. A summary of total emissions from the gasoline refinery module is shown in Table 3.2-1.

3.2.2 Module Description

The crude feedstock for this module is assumed to have a 31° API gravity and a sulfur content of 1.5 wt percent. The heating value of the crude is assumed to be 5.8×10^6 Btu/bbl (BA-230). Characteristics of the crude charge are summarized in Table 3.2-2.

The processing sequences utilized in the gasoline refinery module are given in Figure 3.2-1 along with the major process flow rates. The gasoline refinery has the same basic processing steps as the fuel oil refinery with the addition of the fluidized cat cracking unit and the hydrocracker. These units are employed to achieve the additional cracking capacity necessary for increasing the gasoline product yield. The product yield based upon one barrel of feed is as follows:

. light ends (C_2-C_3),	9.02 lb
. gasoline,	0.625 bbl
. middle distillates,	0.207 bbl
. fuel oil,	0.105 bbl
. coke,	0.875 lb

---

*All flow rates for this module are based on calendar days.

TABLE 3.2-1

SUMMARY OF ENVIRONMENTAL IMPACT

Gasoline Refinery Module

Basis: 200,000 bbl/day Crude Feed

Air (lb/day)	
Particulates	10,380
SO_x	22,750
NO_x	29,990
CO	2,270
Hydrocarbons	76,800
Water (lb/day)	
Suspended Solids	250
Dissolved Solids	9,260
Organic Material	52.5
Solid Wastes (tons/day)	7.0

TABLE 3.2-2

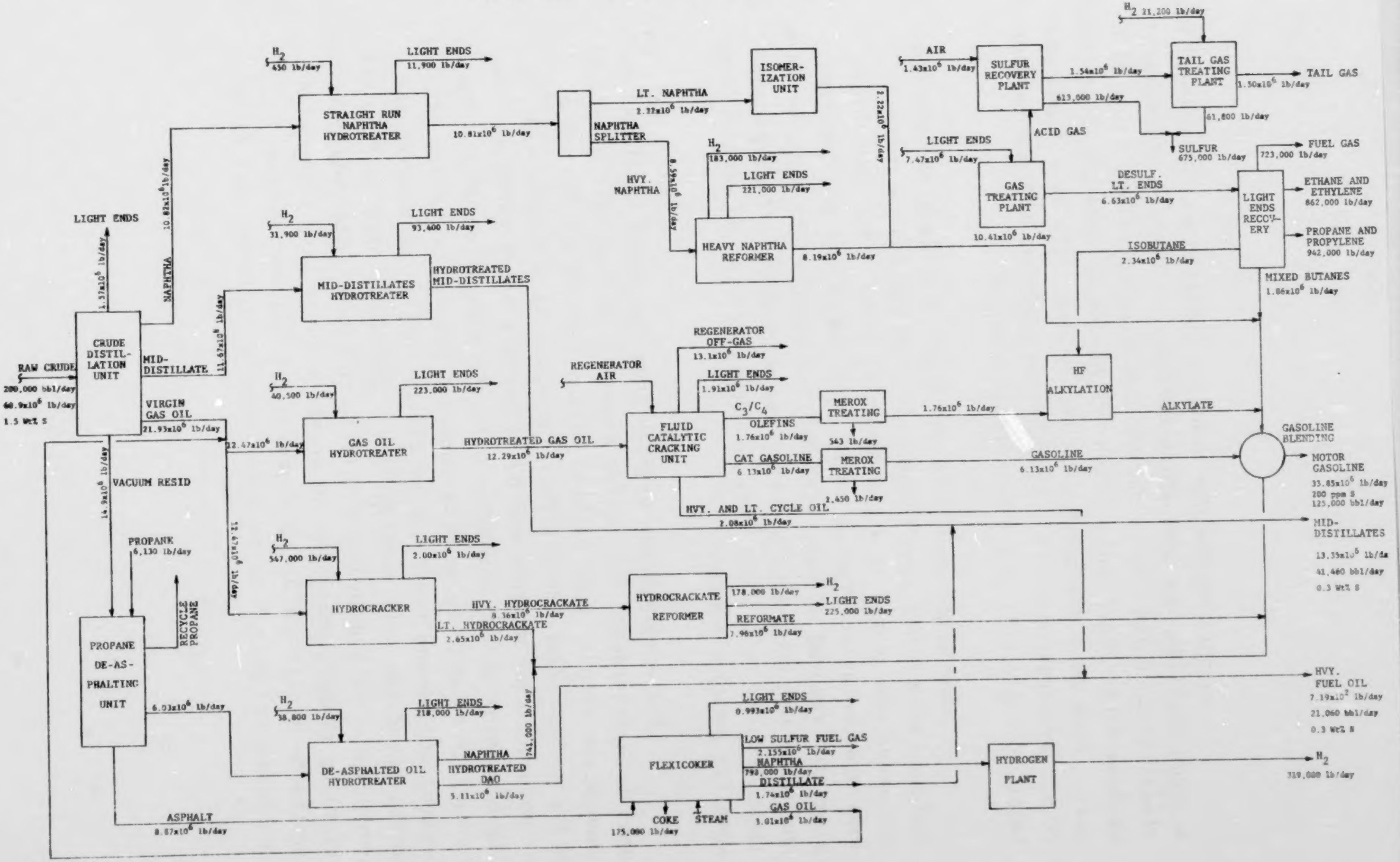
CRUDE FEEDSTOCK CHARACTERISTICS

Gasoline Oil Refinery Module

Crude Characteristics	
API° Gravity	31
Sulfur Content	1.5 wt %
Heating Value	5.8×10^6 Btu/bbl

True Boiling Point Range	wt % of Crude
68/375°F	20.4
375/600°F	19.1
600/1050°F	36.0
1050+°F	24.5

FIGURE 3.2-1 GASOLINE REFINERY MODULE


RAW CRUDE
200,000 bbl/day
$60.9x10^6$ lb/day
1.5 Wt% S
CRUDE DISTIL-LATION UNIT
LIGHT ENDS
$1.57x10^6$ lb/day
NAPHTHA
$10.82x10^6$ lb/day
MID-DISTILLATE
$11.67x10^6$ lb/day
VIRGIN GAS OIL
$21.93x10^6$ lb/day
VACUUM RESID
$14.9x10^6$ lb/day
H_2
450 lb/day
STRAIGHT RUN NAPHTHA HYDROTREATER
LIGHT ENDS
11,900 lb/day
$10.81x10^6$ lb/day
NAPHTHA SPLITTER
LT. NAPHTHA
$2.22x10^6$ lb/day
ISOMER-IZATION UNIT
$2.22x10^6$ lb/day
HVY. NAPHTHA
$8.59x10^6$ lb/day
H_2
183,000 lb/day
LIGHT ENDS
221,000 lb/day
HEAVY NAPHTHA REFORMER
$8.19x10^6$ lb/day
$10.41x10^6$ lb/day
H_2
31,900 lb/day
MID-DISTILLATES HYDROTREATER
LIGHT ENDS
93,400 lb/day
HYDROTREATED MID-DISTILLATES
H_2
40,500 lb/day
GAS OIL HYDROTREATER
LIGHT ENDS
223,000 lb/day
$12.47x10^6$ lb/day
HYDROTREATED GAS OIL
$12.29x10^6$ lb/day
REGENERATOR AIR
FLUID CATALYTIC CRACKING UNIT
REGENERATOR OFF-GAS
$13.1x10^6$ lb/day
LIGHT ENDS
$1.91x10^6$ lb/day
C_3/C_4
OLEFINS
$1.76x10^6$ lb/day
CAT GASOLINE
$6.13x10^6$ lb/day
MEROX TREATING
543 lb/day
MEROX TREATING
2,450 lb/day
$1.76x10^6$ lb/day
HVY. AND LT. CYCLE OIL
$2.08x10^6$ lb/day
AIR
$1.43x10^6$ lb/day
SULFUR RECOVERY PLANT
$1.54x10^6$ lb/day
613,000 lb/day
H_2 21,200 lb/day
TAIL GAS TREATING PLANT
TAIL GAS
$1.50x10^6$ lb/day
61,800 lb/day
SULFUR
675,000 lb/day
ACID GAS
LIGHT ENDS
$7.47x10^6$ lb/day
GAS TREATING PLANT
DESULF. LT. ENDS
$6.63x10^6$ lb/day
LIGHT ENDS RECOV-ERY
FUEL GAS
723,000 lb/day
ETHANE AND ETHYLENE
862,000 lb/day
PROPANE AND PROPYLENE
942,000 lb/day
ISOBUTANE
$2.34x10^6$ lb/day
MIXED BUTANES
$1.86x10^6$ lb/day
HF ALKYLATION
ALKYLATE
GASOLINE
$6.13x10^6$ lb/day
GASOLINE BLENDING
MOTOR GASOLINE
$33.85x10^6$ lb/day
200 ppm S
125,000 bbl/day
MID-DISTILLATES
$13.39x10^6$ lb/da
41,460 bbl/day
0.3 Wt% S
PROPANE
6,130 lb/day
RECYCLE PROPANE
PROPANE DE-AS-PHALTING UNIT
$12.47x10^6$ lb/day
H_2
547,000 lb/day
HYDROCRACKER
LIGHT ENDS
$2.00x10^6$ lb/day
HVY. HYDROCRACKATE
$8.36x10^6$ lb/day
LT. HYDROCRACKATE
$2.65x10^6$ lb/day
HYDROCRACKATE REFORMER
178,000 lb/day
H_2
LIGHT ENDS
225,000 lb/day
REFORMATE
$7.96x10^6$ lb/day
HVY. FUEL OIL
$7.19x10^2$ lb/day
21,060 bbl/day
0.3 Wt% S
$6.03x10^6$ lb/day
H_2
38,800 lb/day
DE-ASPHALTED OIL HYDROTREATER
LIGHT ENDS
218,000 lb/day
NAPHTHA
741,000 lb/day
HYDROTREATED DAO
$5.11x10^6$ lb/day
ASPHALT
$8.87x10^6$ lb/day
FLEXICOKER
LIGHT ENDS
$0.993x10^6$ lb/day
LOW SULFUR FUEL GAS
$2.155x10^6$ lb/day
NAPHTHA
798,000 lb/day
DISTILLATE
$1.74x10^6$ lb/day
GAS OIL
$3.01x10^6$ lb/day
COKE
175,000 lb/day
STEAM
HYDROGEN PLANT
H_2
319,000 lb/day

In this module the crude is desalted and introduced to a crude distillation unit which consists of both an atmospheric distillation column and a vacuum distillation column along with various other flash tanks which are needed to make the distillate cuts. Five cuts are taken from the crudes: (1) sour light ends (C_1-C_4 hydrocarbons), (2) straight run naphtha, (3) middle distillates, (4) gas oil, and (5) residual product.

Sour light ends from the crude distillation unit are combined with other sour light ends from various refinery processes and routed to a gas treating plant. The sour light ends are contacted with an amine solution at the gas treating plant for removal of H_2S. The H_2S is subsequently stripped from the amine and routed to a sulfur recovery unit. The sweetened light ends go to a light ends recovery unit for separation into specific product streams.

The straight run naphtha from the crude distillation unit is hydrotreated for sulfur removal. The naphtha stream is then split into a light naphtha stream (TBP 68-180°F) and a heavy naphtha (TBP 180-375°F). The split is assumed to be 20 wt percent light naphtha and 80 wt percent heavy naphtha. The light naphtha is run through a C_5/C_6 isomerization unit. The isomerization unit is used to increase the octane rating of pentane and hexane fractions by catalytically rearranging the normal paraffins into isoparaffins. The heavy naphtha from the hydrotreater is fed into a catalytic reformer. The catalytic reforming process converts low octane naphtha into high octane naphtha by catalytically rearranging and dehydrogenating naphthenes and paraffins to form benezene, toluene, and xylene.

The products of these two naphtha streams are blended for motor gasoline. The light ends from the catalytic reformer are routed to the gas treating plant, while the hydrogen from the reformer is separated and used in other refinery processes.

The middle distillate cut from the crude distillation unit is also hydrotreated for sulfur removal. The light ends which are produced are sent to the gas treating plant and the product is sent to storage as a hydrotreated middle distillate.

The straight run gas oil cut from the crude distillation unit and the gas oil produced in the flexicoker (discussed later) are combined and then split equally between a hydrocracker and a fluid catalytic cracking unit (FCCU). The gas oil to the FCCU is first hydrotreated to protect the catalyst from poisoning and to reduce SO_2 emissions during catalyst regeneration. The main difference between the products from the two cracking processes is the fact that the hydrocracker products are much more saturated than the products from the FCCU, due to the large amounts of hydrogen utilized in the hydrocracking process.

The FCCU will produce four different product streams. A light ends stream is produced and routed to the gas treating plant for H_2S removal. A C_3/C_4 olefinic cut which is produced is sent to a Merox treating unit for additional sulfur removal by caustic scrubbing and then routed to an alkylation unit. An FCCU gasoline product stream is also treated in a Merox system prior to being routed to the gasoline blending facilities. The combination of heavy and light cycle oil which is produced is routed to storage for a heavy fuel oil product. During the regeneration of the catalyst in the FCCU, a large quantity of off-gas is produced. This off-gas is a major source of air emissions and must be carefully controlled.

The gas oil and hydrogen going into the hydrocracker are converted into essentially two product streams; light ends and a reformer feedstock. The light ends are fed to the gas treating plant for H_2S removal. The hydrocrackate (naphtha) is fed to a catalytic reformer where hydrogen, light ends, and reformate are produced. The hydrogen from the reformer is separated and recycled to the hydrogen consuming refinery processes. The reformer light ends are sent to the gas treating plant, while the reformate is routed to gasoline blending.

The final crude distillation unit product is the vacuum resid. The resid is fed to a propane deasphalting unit where a gas oil is produced by extraction. The deasphalted oil is routed to a hydrotreater for removal of sulfur. The light ends produced in the hydrotreater are routed to the gas treating plant. The remaining product is split into a naphtha stream which goes to the gasoline blending facilities and a hydrotreated, deasphalted oil which is routed to storage as a heavy fuel oil product.

The asphalt from the deasphalting unit is fed to a flexicoker. The flexicoker is a fluid coking process in which the coke product is gasified to produce a usable low Btu fuel gas. The fuel gas is hydrotreated and used as fuel in the propane deasphalting unit. The gas oil produced in the flexicoker is combined with the straight run gas oil from the crude distillation unit and fed to the FCCU and the hydrocracker. The light ends produced are sent to the gas treating plant. The naphtha produced is combined with a portion of the reformate from the straight run naphtha reformer and routed to a hydrogen plant where hydrogen is produced to balance the hydrogen demand within the refinery. The hydrogen plant is a steam-naphtha reforming process. The hydrogen is formed by a multiple-step shift conversion of naphtha and steam into carbon dioxide and hydrogen.

Of the naphtha fed to the hydrogen plant, 37 percent is used for process heater fuel (VO-025).

All the light ends produced by the refinery processes are treated in the gas treating plant and then fed to a light ends recovery unit which splits the stream into: (1) fuel gas, (2) ethane and ethylene, (3) propane and propylene, (4) isobutane, and (5) mixed butanes. The isobutane from the light ends is fed along with the C_3/C_4 olefins from the FCCU to a HF alkylation unit. The olefins and isobutane are catalytically reacted to produce a high octane component for gasoline blending. The mixed butanes from the light ends recovery unit are also blended with the gasoline.

The H_2S from the amine gas treating plant is sent to a sulfur recovery plant for conversion to recoverable sulfur. A Claus plant in conjunction with a tail gas treating unit is used for sulfur recovery. The Claus plant catalytically reacts stoichiometric amounts of H_2S and SO_2 to form sulfur and water. The overall conversion is in the range of 95 percent to 98 percent (HY-014). The tail gas from the Claus plant is treated for additional sulfur removal by washing it with an alkanolamine solution in an absorption column. The final result is greater than 99.8 percent removal of the equivalent sulfur in the original sour acid gas (HY-014).

The liquid wastes resulting from this module are handled in both primary and secondary treatment facilities. The sludge from the water treatment facilities is incinerated. Auxiliary units such as waste water treating facilities and the incinerator are not shown in Figure 3.2-1.

The heat requirements for each unit are calculated from the specific module demands and the calculated flows through each unit. The specific heat requirement for each unit is given on Table 3.2-3. The total module heat requirement is 7.02 x 10^{10} Btu/day.

After the total module heat requirements are established, allocations of the refinery fuels are made. All the fuel gas produced within the refinery is consumed within the refinery. The fuel gas is preferentially used in smaller heaters. However, after the fuel gas has been allocated, 0.3 wt percent fuel oil must be used in the remaining process heaters. Coke gas from the flexicoker is also used as a low Btu fuel gas and fired along with fuel gas in the deasphalting unit process heater. The hydrogen plant heater is fired with naphtha. The heating valves of the various fuels are as follows:

.	Fuel gas	969 Btu/scf	(calculated)
.	Fuel oil	6.3 x 10^6 Btu/bbl	(EN-071)
.	Coke gas	1,598 Btu/lb	(FL-047)
.	Naphtha	5.248 x 10^6 Btu/bbl	(EN-071)

The fuels used in the specific unit process heaters are given in Table 3.2-3.

TABLE 3.2-3
GASOLINE REFINERY
MODULE HEAT REQUIREMENTS

Unit	Unit Heat Requirement (Btu/day)	Fuel Used
Crude Unit	2.0×10^{10}	Fuel Oil
Mid-Distillate Hydrotreater	2.14×10^{9}	Fuel Gas
St. Run Naphtha Hydrotreater	8.53×10^{8}	Fuel Gas
Heavy Naphtha Reformer	1.078×10^{10}	Fuel Oil
Gas Oil Hydrotreater	2.13×10^{9}	Fuel Oil
FCCU	5.89×10^{9}	Fuel Gas
Hydrocracker	6.20×10^{9}	Fuel Gas
Hvy. Hydrocrackate Reformer	1.07×10^{10}	Fuel Oil
Propane Deasphalting	3.68×10^{9}	Coke Gas & Fuel Gas
Deasphalted Oil Hydrotreater	1.39×10^{9}	Fuel Gas
HF Alkylation	2.1×10^{7}	Fuel Gas
C_5/C_6 Isomerization	6.81×10^{8}	Fuel Oil
Light Ends Recovery	2.01×10^{7}	Fuel Gas
Tail Gas Treating	1.50×10^{8}	Fuel Gas
Hydrogen Plant	5.72×10^{9}	Naphtha

3.2.3 Module Emissions

3.2.3.1 Air Emissions

Air emissions from the gasoline refinery module result from fuel combustion, CO boiler, sulfur recovery, steam-hydrocarbon reforming (hydrogen plant), sludge incineration, petroleum storage, and miscellaneous hydrocarbon emissions. Module air emissions from the specific sources are given in Table 3.2-4.

Fuel Combustion Emissions

Utilizing fuel demand data for the various processes, fuel combustion emission sources are determined to be the following (HY-013, HY-014, VO-025):

- crude distillation
- middle distillate hydrotreater
- straight run naphtha hydrotreater
- heavy naphtha reformer
- gas oil hydrotreater
- fluidized catalytic cracking unit
- CO boiler
- hydrocracker
- heavy hydrocrackate reformer
- propane deasphalting unit
- deasphalted oil hydrotreater
- HF alkylation
- C_5/C_6 isomerization
- light ends recovery
- tail gas treating plant
- hydrogen plant

TABLE 3.2-4

MODULE ATMOSPHERIC EMISSIONS

GASOLINE REFINERY MODULE

(lb/day)

Basis: 200,000 bbl/day Crude Feed

	Particulates	SO_x	CO	Hydrocarbons	NO_x
Crude Distillation	3,080	6,400	533	533	5,330
Mid-Distillate H.T.	45	64	38	65.4	518
St. Run Naphtha H.T.	18	26	15	25.7	207
Hvy. Naphtha Reformer	1,660	3,560	287	288	2,870
Gas Oil Hydrotreater	326	703	57	56	567
FCCU	124	176	106	181	1,425
CO Boiler	491	3,020	256	160	6,370
Hydrocracker	131	185	110	1,077	1,110
Hvy. Hydrocrackate Reformer	1,650	3,540	285	286	2,854
Propane Deasphalting	622	884	48	81	656
Deasphalted Oil H.T.	29	42	25	42	336
HF Alkylation	0.4	0.6	0.4	0.7	5
Light Ends Recovery	11	15	9.2	15.7	125
C_5/C_6 Isomerization	105	225	18.5	18.2	181
Hydrogen Plant	1,720	345	344	338	6,890
Storage					
1) Crude	-	-	-	7,550	-
2) Motor Gasoline	-	-	-	5,050	-
3) Mid-Distillates	-	-	-	97	-
4) Hvy. Fuel Oil	-	-	-	Neg.	-
Sludge Incineration	361	600	133	42	510
Tail Gas Treating	3.1	Tail Gas 3,560	2.6	4.6	36
Miscellaneous	-	-	-	60,900	-
TOTAL	10,380	22,750	2,270	76,800	29,990

Although each unit may contain several fuel combustion emission sources, all flue gas streams within one unit are assumed to be combined and routed to one stack. Therefore, each unit requiring fuel combustion represents one emission source. The emissions from each unit are based on the type of fuel used, such as fuel gas, fuel oil, or coke gas, and the EPA emission factors. All of the fuel combustion emission factors are shown in Table 3.2-5. The SO_x emissions from the fuel oil are calculated using a sulfur content of 0.3 wt percent. The SO_x emissions from combustion of fuel gas are calculated assuming the H_2S concentration in the fuel gas is in compliance with the Federal regulation of 0.10 grains per dscf (ST-124).

The steam-hydrocarbon reforming has special emission factors due to the high operating temperature (1700°F) of the process heater which tents to enhance the formation of NO_x. Special emission factors must also be used because naphtha instead of fuel oil or fuel gas is used in the process heaters (AT-040).

Due to the different composition of the coke gas, estimated values for the coke gas emission factors had to be determined. The particulates emission factor is assumed to be the same as for fuel gas. The SO_x emission factor is also assumed the same and based on a hydrogen sulfide concentration in compliance with the Federal standard of 0.10 grain H_2S per dscf (ST-124). The emission factor for CO, hydrocarbons, and nitrogen oxides are determined by multiplying the EPA emission factors for each of these constituents for fuel gas by the ratio of the heating value of the coke gas to the heating value of the fuel gas (EN-071).

TABLE 3.2-5
EMISSION FACTORS FOR GASOLINE REFINERY FUEL USE

Air Pollutant	Fuel Gas lb/1000 scf	Fuel Oil lb/barrel	Coke Gas[4] lb/1000 scf	Steam-Hydrocarbon Reforming (lb/1,000 scf)
Particulates	0.02	0.97	0.02	0.84[5]
Sulfur Oxides (SO_x)	2 x S_G[1]	6.72 x S_O[2]	2 x S_G[1]	6.72 x S_N[3]
CO	0.017	0.168	0.0013	0.168
Hydrocarbons	0.029	0.168	0.0022	0.165[5]
Nitrogen Oxides (NO_x)	0.23	1.68	0.018	3.36

---

[1] S_G is Equal to the Sulfur Concentration of the Gas.

[2] S_O is Equal to the Weight Percent Sulfur in the Fuel Oil.

[3] S_N is Equal to the Weight Percent Sulfur in the Naphtha Fuel.

[4] Calculated using EPA Emission Factors and the Ratio of Coke Gas to Fuel Gas Heating Values.

[5] Reference (AT-040)

Source: (EN-071)

CO Boiler

The CO boiler flue gas rate is estimated at 64,000 scfm (CU-016). Emissions from the CO boiler are calculated as follows:

(1) Particulates are calculated to be the maximum allowed by Federal emission laws, 0.027 gr/dscf (EN-196).

(2) SO_2 emission is calculated assuming the sulfur in the coke (on the FCCU catalyst) is 0.21 wt percent of the coke, and all the sulfur in the coke is converted to SO_2.

(3) The hydrocarbon emission factor used was based on the assumption that the concentration of the hydrocarbons in the flue gas is equal to the hydrocarbon concentration in the flue gas from the combustion of residual oil. This concentration is 1.65×10^{-6} lb/scf of flue gas, and includes aldehyde emissions.

(4) The regenerator flue gas entering the CO boiler contains 71 lb NO_x/1,000 bbl of cat cracker feed and 54 lb NH_3/1,000 bbl of cat cracker feed (EN-071). In a CO boiler, it is assumed that the only NO_x formed in the CO boiler is from the combustion of NH_3 to NO_x. With these premises, a NO_x emission factor for CO boilers of 166 lb NO_x/1,000 bbl cat cracker capacity, based upon total combustion of NH_3 to NO, was used.

(5) The emission factor used for calculating the CO emission from the module CO boiler is

20 ppm of the boiler flue gas. This factor is based on a survey for EPA which reported 20 ppm to be the average CO concentration in the CO boiler flue gas (EN-072).

Sulfur Recovery

The efficiency of sulfur removal by the sulfur recovery plant and the tail gas treating plant is approximately 99.8 percent (HY-014). The 0.2 percent not recovered is exhausted as SO_2 at a rate of 3,390 lb/day. The tail gas is routed to a stack within the refinery.

Steam-Hydrocarbon Reforming (Hydrogen Plant)

Due to the high operating temperature (approximately 1700°F) of the steam-hydrocarbon reforming plant, special emission factors must be used. The high temperatures that must be achieved within the heater place a limit on the degree of NO_x emission control that can be practiced through modification of combustion techniques. The emission factors for steam-hydrocarbon reforming are listed in Table 3.2-5.

Sludge Incineration

The oily sludge from the API separator and the biological sludge from the waste treatment facilities are both incinerated. The quantity of oil incinerated in the oily sludge is based on the following (MA-226).

(1) 0.0015 bbl of oily sludge/bbl crude throughput is produced,

(2) the oily sludge is 36.6 wt percent oil, and

(3) the weight of the sludge is 340 lb/bbl.

The emissions from burning the oily sludge are based on the assumption that the oil in the sludge has the same characteristics of fuel oil and thus the same emission factors. These emission factors are shown in Table 3.2-6.

The biological sludge produced within the refinery is calculated to be 4,750 lb/day. This value is based on the following:

(1) 10,000 lb BOD removed/day (US-056),

(2) 0.5 lb volatile solids formed/lb of BOD removed (BE-047), and

(3) The BOD removal efficiency is 95 percent (BE-047).

The emission factors used for biological sludge are the EPA emission factors for municipal wastes incineration (EN-071). These factors are also given in Table 3.2-6.

Petroleum Storage

In order to calculate the hydrocarbon emissions from petroleum storage, the following assumptions are used:

(1) Storage capacity is one month for feed and products,

(2) Only crude and gasoline storage will result in significant hydrocarbon emissions. Light fuel oil storage will result in a small hydrocarbon emission,

TABLE 3.2-6
SLUDGE INCINERATION EMISSION FACTORS

Pollutant	Oily Sludge lb Emission/1,000 gal Sludge	Biological Sludge lb Emission/Ton
Particulates	23	30
SO_2	47	2.5
CO	4	35
Hydrocarbons	3	1.5
NO_x	40	3

Source: (EN-071)

(3) Heavy fuel oil storage and pressurized storage of high volatility products will result in negligible emission, and

(4) Crude, gasoline, and fuel oils will be stored in floating-roof tanks.

Hydrocarbon emission factors for floating roof tanks are the following (EN-071):

.	crude oil	0.029 lb/day-10^3 gal
.	gasoline	0.033 lb/day-10^3 gal
.	light fuel oil	0.0052 lb/day-10^3 gal

Miscellaneous Hydrocarbon Emissions

There are numerous miscellaneous hydrocarbon emissions in petroleum refineries which escape from sources such as valve stems, flanges, loading racks, equipment leaks, pump seals, sumps, drains, sewers, ruptured discs, and API separators. Based on literature data, these mescellaneous hydrocarbon emissions amount to about 0.1 percent of the refinery capacity for a new, well-designed, well-maintained refinery (RA-119). The composition of these hydrocarbons can be expected to be a composite of all volatile intermediate and refined products.

3.2.3.2 Water Effluents

Module water effluents have been estimated from published information (RA-119). The wastewater generation rate is taken as 15 gallons per barrel of crude feed. This value is believed to be reasonable considering modern water conservation techniques, segregation of wastewater streams, air cooling, and recycle. The concentrations of the pollutants are based on the efficiencies of primary and secondary wastewater treatment facilities. The concentrations of pollutants in the effluent are given in Table 3.2-7.

3.2.3.3 Solid Wastes

The solid wastes from a refinery are highly variable. Possible sources of solid wastes in a refinery are the following:

(1) entrained solids in the crude,

(2) silt from surface drainage,

(3) silt from water supply,

(4) corrosion products from process units and sewer systems,

(5) solids from maintenance and cleaning operations,

(6) water treatment facilities, including ash from the sludge incinerator, and

(7) spent catalyst.

With the exception of spent catalyst, the solids collect in the API separator and the waste water treating facilities. The solid wastes are estimated at seven tons per day. Three of the

TABLE 3.2-7

WASTEWATER EFFLUENT QUALITY

Gasoline Refinery Module

Basis: 200,000 bbl/day Crude Feed

Flow Rate - 3.0×10^6 gal/day

	Concentration
BOD	15 ppm
COD	80 ppm
Ammonia	2 ppm
Hydrogen Sulfide	0.1 ppm
Total Phosphorous	2 ppm
Phenol	0.1 ppm
Oil	2 ppm
Suspended Solids	10 ppm
Dissolved Solids	370 ppm

Source: (RA-119)

seven tons are from the solid wastes from the API separator and the waste water treatment facility. THe other four tons are from spent catalyst from the cat cracker and the hydrodesulfurization units and are only averages of the intermittent catalyst regenerations.

3.3 LNG Module

LNG facilities in service or under construction throughout the world are designed for either peak-shaving or base load applications. Most plants in the U.S., though, are designed for peak-shaving operations. These peak-shaving plants were developed to satisfy an area's peak gas demand at the times when the natural gas supply would be insufficient. At such times, liquefied natural gas from a peak-shaving plant could be withdrawn from storage, regasified, and fed into the distribution lines. During periods when the potential supply exceeds the demand, surplus natural gas may be liquefied and stored. With this type of approach, a significant natural gas storage capability can be provided. Currently, there are fifty-five such peak-shaving plants in operation in the U.S. They range in size from 5 x 10^5 scfd to 25.0 x 10^6 scfd of liquefaction capacity.

3.3.1 Peak-Shaving Module

The basis for the LNG module is a typical size peak-shaving plant operating in the U.S. The liquefaction capacity of the module is 10 x 10^6 scfd* of pipeline natural gas. All emissions determined for this module are based on this liquefaction capacity. A summary of emissions from the plant is presented in Table 3.3-1.

3.3.1.1 Peak-Shaving Module Description

In this section, the processing steps utilized in the LNG module are briefly discussed. These processes include acid

---

* All flow rates in this module are based on calendar days.

TABLE 3.3-1

SUMMARY OF ENVIRONMENTAL EMISSIONS
LNG MODULE

Basis: 10×10^6 scfd of Natural Gas Liquefied

Air (lb/day)	
Particulates	59
SO_2	7.9
NO_x	758
HC	470
CO	56
Water (lb/day)	
Suspended Solids	0
Dissolved Solids	0
Total	0
Solids (tons/day)	0

gas removal, dehydration, liquefaction, storage, and regasification. A flow diagram is shown in Figure 3.3-1 illustrating the processing sequence.

Processing Steps

To insure that no solids form in the cold box during methane liquefaction, the incoming stream to the plant must first be treated for the removal of CO_2 and H_2O. In industry today, molecular sieves are by far the most popular unit for handling this clean-up job. They easily purify the natural gas feedstock to less than 1 ppm H_2O and less than 50 ppm CO_2. At the same time, they also remove most of the sulfur compounds present in the feed stream (H_2S, COS, CS_2, and mercaptans).

A two-bed molecular sieve unit is used in this module for acid gas and H_2O removal. One bed is on-line absorbing while the other is being regenerated. A gas-fired heater is required to heat the gas for molecular sieve regeneration. This heater consumes 5,000 Btu per hour per million scfd of gas treated (IN-029). The quantity of gas needed for regeneration is typically around 2% of the daily throughput of the sieves. The gas resulting from molecular sieve regeneration contains higher concentrations of sulfur, CO_2, and H_2O. This gas is combined with fuel to the boilers in order to supply module heat requirements. The molecular sieve operates at 1 atm pressure and at the temperature of the incoming gas, usually ambient (HA-274).

After passing through the molecular sieve bed, the natural gas composition is:

Methane	-	98%
Ethane	-	1%
Propane	-	0.5%
Nitrogen	-	0.5%

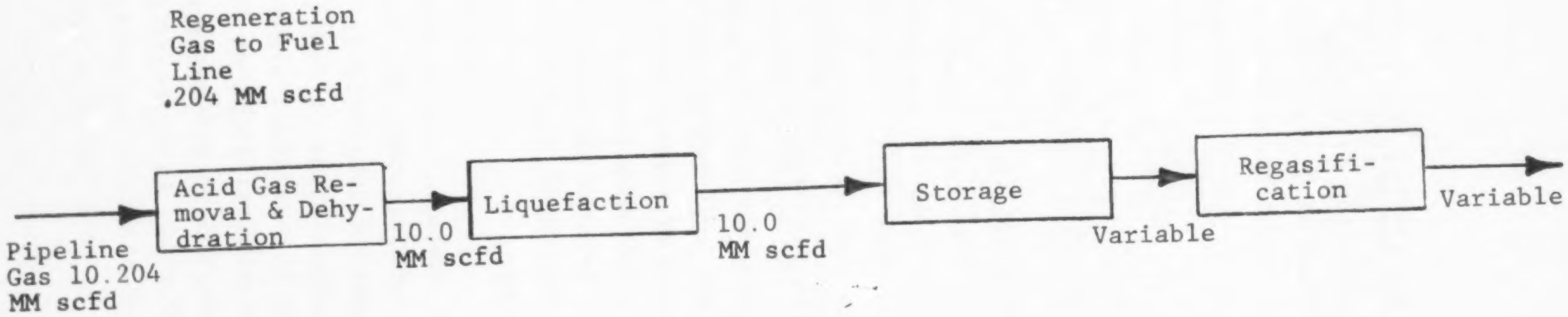

Regeneration Gas to Fuel Line .204 MM scfd
Pipeline Gas 10.204 MM scfd
Acid Gas Removal & Dehydration
10.0 MM scfd
Liquefaction
10.0 MM scfd
Storage
Variable
Regasification
Variable

FIGURE 3.3-1 LNG PEAK-SHAVING PLANT - 10 MM SCFD CAPACITY

Liquefaction of the methane stream is the next step in the LNG plant. Liquefaction is accomplished with a single mixed refrigerant liquefaction cycle. The mixed refrigerant, composed of nitrogen and light hydrocarbons from methane through pentane, is circulated in a closed refrigeration loop. This loop contains a compressor, a partial condenser, a refrigerant heat exchanger, and a Joule-Thompson expansion valve. The power to drive the compressor requires approximately 13% of the gas charged to the liquefaction unit (IN-029).

LNG storage is accommodated in an above-ground double walled metallic tank with a storage capacity of 2.0 x 10^9 scf. Normal boiloff due to heat leaks is approximately 0.040% of the tank capacity per day when full. The boiloff gas is compressed and routed to the distribution system. The storage tank is operated at atmospheric pressure.

The regasification system is a submerged combustion type with a maximum sendout capacity of 200 MM scfd. Approximately 2% of the gas vaporized must be combusted to supply the necessary heat (IN-029). For this module it is assumed that pipeline natural gas will be used to supply this heat requirement.

Module Flow Rates

For this module, natural gas is fed to the plant at a rate of 13.502 MM scfd. Before this gas enters the molecular sieves for cleanup, a stream is taken off at the rate of 3.298 MM scfd to supply fuel for the plant.

This leaves a stream of 10.204 MM scfd entering the molecular sieve unit. A small stream amounting to 2% of this unit's throughput, 204,000 scfd, is diverted from the downstream side of the molecular sieve beds and heated for use as a regeneration gas. This gas is then fed into the fuel line for use as plant fuel.

After cleanup, the gas stream passes into the liquefaction unit at the rate of 10 MM scfd. After liquefaction, the natural gas is pumped to a 2 billion scf capacity storage tank.

The regasifier is designed for a maximum sendout capacity of 200 MM scfd. Combining with this amount the daily boiloff rate of 800,000 scfd from the LNG tank, the maximum output from this module is 200.8 MM scfd. However, this large discharge rate is used only in times of peak gas demand. For the purpose of this module, the environmental effect of regasification will be based upon a sendout rate of 100 MM scfd.

Module Heat Requirements

Overall module heat requirements are determined from process unit utility requirements and flow rates. The heat requirements for the various process units are presented in Table 3.3-2. The total module heat requirement is 3.30 x 10^9 Btu/day. This heat requirement is supplied by pipeline gas (94%) and molecular sieve regeneration gas (6%).

3.3.1.2 Peak-Shaving Module Emissions

Air Emissions

Atmospheric emission sources within the natural gas liquefaction module include the flue gases from: (1) the boiler which supplies power to the liquefaction train compressors, (2) the molecular sieve regeneration gas heater, and (3) the regasifier, as well as miscellaneous fugitive hydrocarbon emission sources. A summary of the air emissions is presented in Table 3.3-3.

TABLE 3.3-2

MODULE HEAT REQUIREMENT

Basis: 10 MM scfd of natural gas liquefied.

Unit	Heat Requirement per MM scf Charge (M Btu/MM scf)	Flow Rate (MM scfd)	Unit Heat Requirement (Btu/day)
Molecular Sieves	120	10.204	$.01 \times 10^8$
Liquefaction Compressor	130,000	10.000	13.00×10^8
Regasifier	20,000	100.000	19.97×10^8
			32.98×10^8

TABLE 3.3-3

SUMMARY OF LNG MODULE AIR EMISSIONS

Module Basis: 10 MM scfd Natural Gas Liquefied

PROCESS	PARTICULATES	POLLUTANTS EMITTED (lbs/day) SO_2	 NO_x	 HC	 CO
Liquefaction Unit Boiler	23.4	7.8	299.0	3.9	22.1
Regasifier	35.9	0.1	459.3	6.0	34.0
Fugitive Hydrocarbon Losses	-	-	-	460	-
TOTAL	59.3	7.9	758.3	469.9	56.1

Stack gas emission rates for the liquefaction unit boiler are calculated using EPA emission factors for natural gas-fired industrial boilers (EN-071). These factors are used since the boiler required by the LNG module is equivalent in size to industrial boilers. The emission factors used are presented in Table 3.3-4. The SO_2 factor includes the extra 7.8 lbs/day of SO_2 formed by the combustion of the higher sulfur content molecular sieve regeneration gas in the boiler. The EPA emission factors for a small industrial boiler are used to determine emissions from the regasifier. These emission factors are also presented in Table 3.3-4. The molecular sieve regeneration gas heater does require natural gas to be burned as its heat source. However, as can be seen from Table 3.3-2, the amount of gas needed per day is very small, and so its emissions are negligible.

Miscellaneous fugitive hydrocarbon emission sources result from process leaks at pump seals, valve stems, flanges, etc. The quantity of these emissions is dependent upon the amount of attention given to plant maintenance. Thus, it is difficult to estimate these hydrocarbon losses; however, it was assumed that 0.1 weight percent of the plant throughput is a reasonable estimate. The daily amount emitted for this module is shown in Table 3.3-3.

Liquid Effluents

The boiler make-up feed water for the plant is first passed through an ion exchange resin unit for demineralization. Regeneration of this unit with acid and caustic wash water streams results in this module's only significant liquid effluent stream. This stream is discharged into holding ponds on the plant site where the water is evaporated. Since no liquid leaves the plant boundaries, the module wastewater effluent is considered to be zero.

TABLE 3.3-4

EMISSION FACTORS FOR LNG MODULE

PROCESS	PARTICULATES	SO_2	EMISSION FACTOR (lb/10^6 scf)[2] NO_x	HC	CO
Liquefaction Unit Boiler	18	6[1]	230	3	17
Regasifier	18	.06	230	3	17

[1] Includes the sulfur from the molecular sieve regeneration gases.

[2] SOURCE: (EN-071)

Solid Wastes

An LNG plant has no solid wastes generated by any of its processes.

3.3.2 Base Load Module

The base load liquefaction scheme was designed as a means for correcting a supply/demand imbalance through the liquefaction and transportation of large amounts of natural gas to centers of consumption. These operations strongly resemble those of a peak-shaving liquefaction scheme, though usually on a larger scale.

The basis for the base load LNG module is a plant which has a liquefaction capacity of 750 MM scfd* of natural gas. All emissions calculated for this module are based on this liquefaction rate. A summary of the module emissions is shown in Table 3.3-5.

3.3.2.1 Base Load Module Description

In this section, the processing steps utilized in the base load module are briefly discussed. These processes include, in order, liquid knock-out, acid gas removal, dehydration, final purification, heavy hydrocarbon recovery, liquefaction, storage/transportation, and revaporization. A flow diagram is presented in Figure 3.3-2 illustrating the process sequence.

Processing Steps

The natural gas feed to the plant has had little processing, therefore, extensive treatment of the gas is needed

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* All flow rates in this module are based on calendar days.

TABLE 3.3-5

SUMMARY OF ENVIRONMENTAL EMISSIONS

BASE LOAD LNG MODULE

Basis: 750 MM scfd Liquefaction Capacity

Air (lb/day)	
Particulates	1,770
SO_2	8,460
NO_x	62,000
HC (including TEG*)	32,560
CO	1,910
Water (lb/day)	0
Solids (tons/day)	0

---

* Triethylene Glycol

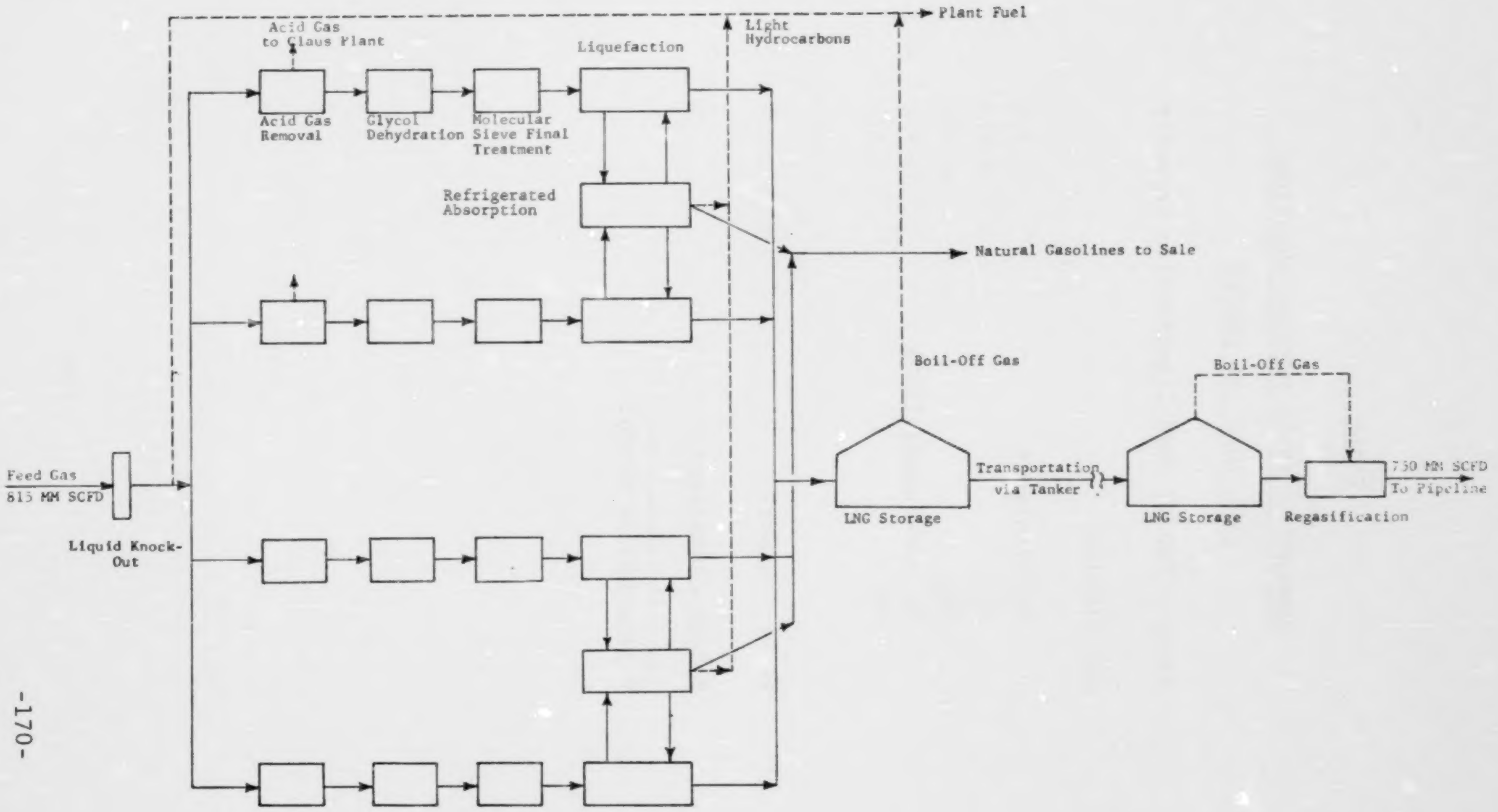
Feed Gas
815 MM SCFD
Liquid Knock-Out
Acid Gas to Claus Plant
Acid Gas Removal
Glycol Dehydration
Molecular Sieve Final Treatment
Liquefaction
Refrigerated Absorption
Light Hydrocarbons
Plant Fuel
Natural Gasolines to Sale
Boil-Off Gas
LNG Storage
Transportation via Tanker
Boil-Off Gas
LNG Storage
Regasification
750 MM SCFD
To Pipeline

FIGURE 3.3-2 LNG BASE LOAD PLANT

prior to its liquefaction. The first unit encountered by the incoming gas is a liquid knock-out to remove any water or heavy hydrocarbons which may have condensed in the pipeline during transmission. After removal of liquids, the gas enters a Girbitol unit where a lean monoethanolamine solution removes the bulk of the acid gases in a packed tower. The H_2S containing gases removed from the top of amine regeneration are sent to a Claus sulfur recovery plant. After this treatment the natural gas is saturated with water. A glycol unit utilizing triethylene glycol contacts the wet gas with the hygroscopic liquid in a bubble tray column. Here the gas gives up the bulk of its water vapor to the glycol and passes out the top of the tower to further processing.

To insure that no solids form in the cold box during liquefaction, the gas needs further conditioning for the removal of CO_2, H_2O, and H_2S to acceptable levels. A molecular sieve unit is used to remove to trace levels the quantities of these contaminants which were present after amine and glycol treating.

Still present in the clean natural gas, though, are significant fractions of heavier hydrocarbons which may freeze out during liquefaction. These are removed in a refrigerated absorption system using heavier hydrocarbons as the solvent. The bottoms from the benzene column which still contain lighter fractions are fed to the refrigerant-makeup units. These units, each consisting of a demethanizer, deethanizer, depropanizer, and debutanizer column, yield hydrocarbon fractions suitable for makeup of refrigerant losses and a light gasoline. Production in excess of refrigerant losses is injected into LNG as far as quality permits. The balance of the light hydrocarbons are used as plant fuel gas. The light gasoline is transferred to an oil company via pipeline.

Liquefaction of the methane stream exiting from the refrigerated absorption unit is the next processing step. The mixed refrigerant cycle (MRC) process is used for liquefying the natural gas. The coolant used consists of a mixture of hydrocarbons extracted from the natural gas and nitrogen.

Following liquefaction, the LNG is pumped to either of two, 2 billion scf capacity above-ground metal tanks. These tanks hold the LNG prior to the arrival of an LNG tanker for shipment to a designated receiving terminal.

The tankers are used to move large volumes of LNG from the liquefaction plant to a purchaser. Upon arrival at the receiving terminal, the LNG is unloaded from the tankers and stored in either of two, 2 billion scf capacity metal above-ground tanks. These storage tanks hold the LNG until it is regasified for distribution to the gas mains.

Module Flow Rates

Natural gas from the field is supplied to the plant at the rate of 815 MM scfd. Approximately 91 percent of the feed is methane, with the remainder being heavier hydrocarbons, carbon dioxide, water vapor, sulfur compounds, and nitrogen. After processing and conditioning the gas is fed to the liquefaction units at the rate of 750 MM scfd. Of this gas, roughly 98 percent is methane with the remainder being mostly ethane and some propane. The LNG is pumped to storage from the liquefaction unit at the rate of 750 MM scfd. From there it is loaded onto LNG tankers for transport to the receiving terminal. At the receiving terminal, the LNG is withdrawn from storage and regasified at the rate of 750 MM scfd.

Module Heat Requirement

Based on a liquefaction and regasification rate of 750 MM scfd and assuming that 13% of the gas throughput to the liquefaction unit is required as fuel to the plant and 2% of the throughput to the regasifiers is needed as heat input to vaporize the LNG, the module heat requirement is 1.125×10^{11} Btu/day. The heat requirement at the plant is supplied by boil-off gas from storage, gas from process units (mainly separated heavy hydrocarbons), and fresh gas from the incoming feed. Roughly 40% of this plant fuel is supplied by the unprocessed fresh gas. Assuming a sulfur content in the field gas of 0.5 volume percent, the boilers will be burning a gas with a 0.20 volume percent sulfur composition.

3.3.2.2 Base Load Module Emissions

Air Emissions

Atmospheric emission sources within the natural gas base load liquefaction module include the flue gases from: (1) the boiler plant which supplies steam for the various clean-up, hydrocarbon recovery, and liquefaction processes, as well as providing steam for driving turbines of compressors, electric-power generators and pumps, (2) the regasifier, (3) the Claus plant, and (4) the glycol system. Also, there are miscellaneous fugitive hydrocarbon emissions from within the liquefaction plant. A summary of the air emissions is presented in Table 3.3-6.

Stack gas emissions rates for the plant boilers are calculated using EPA emission factors for natural gas-fired utility size boilers (EN-071). These factors are used since the boilers used in this module are similar in size to a utility boiler. These emission factors are presented in Table 3.3-7.

TABLE 3.3-6

SUMMARY OF LNG BASE LOAD MODULE AIR EMISSIONS

Module Basis: 750 MM scfd of Natural Gas
Liquefied

PROCESS	Pollutants Emitted (lbs/day) PARTICULATES	SO_2	NO_x	HC	CO	TEG
Plant Boilers	1,500	8,290	58,500	98	1,658	-
Glycol Unit						370
Regasifier	270	0	3,450	45	255	-
Claus Plant	-	172	-	-	-	-
Fugitive Hydrocarbon Losses	-	-	-	32,000	-	-
TOTAL	1,770	8,462	61,950	32,193	1,913	370

TABLE 3.3-7

EMISSION FACTORS FOR LNG MODULE

Emission Factor ($lb/10^6$ scf)

PROCESS	PARTICULATES	SO_2	NO_x	HC	CO
Plant Boilers	15	85[1]	600	1	17
Regasifier	18	0[2]	230	3	17

---

[1] Factor includes sulfur present in feed gas used for fuel which has not been treated.

[2] Sulfur-free fuel used.

The regasifier emissions were determined using factors for a large industrial boiler (EN-071). These factors are given in Table 3.3-7. Since the regasifier is fired from sulfur-free storage boil-off and vaporized LNG, there are no sulfur dioxide emissions.

The tail gas from the Claus plant containing unconverted H_2S and other sulfur compounds is treated by the Beavon tail gas treatment process. It removes the sulfur in the tail gas to a concentration of 250 ppm (SO_2) or lower before discharge to the atmosphere (RA-119). The daily emission rate of SO_2 from the Claus plant is presented in Table 3.3-6.

In the operation of the glycol dehydration unit, water vapor is continuously vented from the triethylene glycol (TEG) regenerator column. Through this vent stream it is reported that 0.05 gallons of TEG per MM scf of gas processed is lost to the atmosphere (PR-052). The daily discharge rate of TEG is given in Table 3.3-6.

Miscellaneous fugitive hydrocarbon emissions result from process leaks at pump seals, valve stems, flanges, etc. The quantity of these emissions is dependent upon the amount of attention given to plant maintenance. Thus, it is difficult to estimate these hydrocarbon losses; however, it was assumed that 0.2 weight percent of the plant throughtout is a reasonable estimate. Table 3.3-6 gives the estimated amount lost daily.

Liquid Effluents

The majority of the liquid effluent generated by the module is from the acid and caustic wash water streams used for the demineralizer regeneration. It is assumed that these streams, as well as other liquid waste streams, are processed at a central water treatment plant. The liquid from this plant is then discharged to one of three containment/evaporation ponds. Since the ponds are located within plant boundaries, the module wastewater effluent is reported to be zero.

Solid Wastes

There are no solid wastes generated within this module which will cause a solids handling problem.

3.4 SNG Module

Increasing demand, combined with declining reserves and exploration, have resulted in significant natural gas shortages in the United States. These trends have encouraged gas producers to seek a reliable and efficient means to produce substitute natural gas to augment the slowly dwindling gas supplies. Current technology is available to gasify liquid feedstocks ranging from LPG to crude oil on a commercial scale. However, government allocation programs and official policy is to limit feedstocks to naphtha only (FE-085). Currently there are 13 SNG plants built or under construction in the U.S. Plant size ranges from an SNG output of 20 MM scf per day to 250 MM scf per day.

3.4.1 Module Basis

The basis for the SNG module is a typical medium-sized plant operating in the U.S. The gasification potential is 125 MM scf per day* of pipeline quality natural gas. All emissions for this module are determined based on this gasification capacity. Table 3.4-1 summarizes the emissions resulting from this module.

3.4.2 Module Description

In this section, the processing steps utilized in the SNG module are briefly discussed. Figure 3.4-1 presents a flow disgram of the processing sequence chosen for this module. These processes include naphtha hydrodesulfurization, gasification in a Catalytic Rich Gas (CRG) reactor, methanation (two stages), CO_2 removal, dehydration, and hydrogen production.

---

*All flow rates in this module are based on calendar days.

TABLE 3.4-1
SUMMARY OF ENVIRONMENTAL IMPACT
SNG PLANT MODULE

Basis: 125 MM scfd of SNG produced

Air (lb/day)	
Particulates	469.4
SO_2	202.7
NO_x	5,216.1
HC (including TEG*)	16,241.8
CO	229.1
Water (lb/day)	0
Solid (lb/day)	negligible

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* Triethylene Glycol

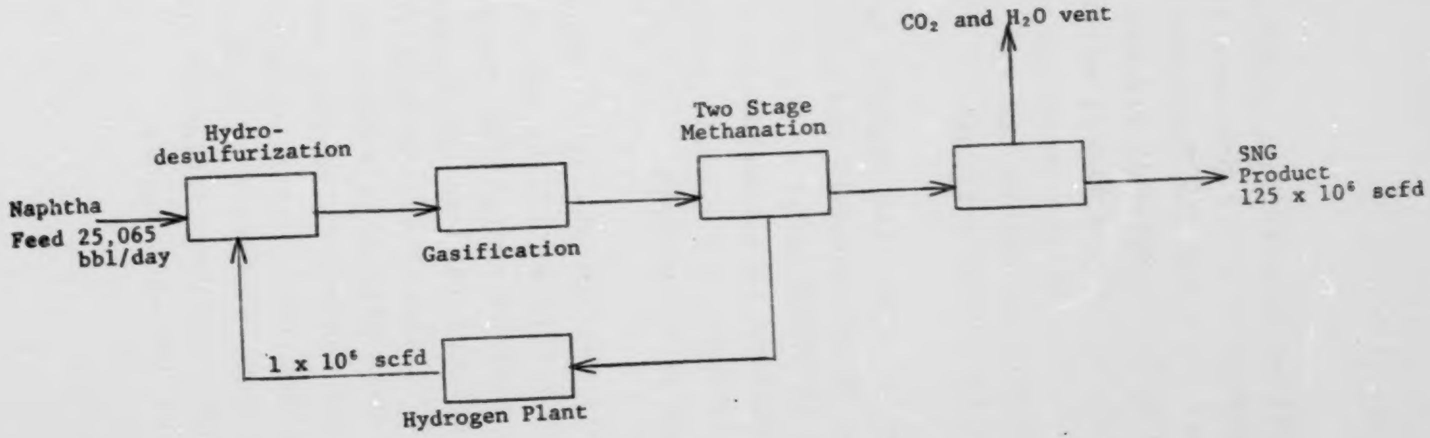
CO₂ and H₂O vent
Hydro-
desulfurization
Two Stage
Methanation
Naphtha
Feed 25,065
bbl/day
Gasification
SNG
Product
125 x 10⁶ scfd
1 x 10⁶ scfd
Hydrogen Plant

FIGURE 3.4-1 SNG MODULE PROCESSING SEQUENCE

Processing Steps

The first step involved in gasifying naphtha is the reduction of sulfur in the charge to a 0.2 ppm concentration. This reduction is accomplished in a naphtha hydrodesulfurization unit, which hydrogenates the sulfur compounds present in the vaporized feed to hydrogen sulfide over a nickel molybdenum catalyst. Following the hydrotreating the vaporized naphtha is routed through a bed of zinc oxide to remove the H_2S. The H_2S reacts with the zinc oxide to form zinc sulfide.

After this purification step, the naphtha is mixed with steam (2 lbs of steam per lb of naphtha) and heated in a superheater to a temperature of 850°F prior to entering the CRG reactor. In this vessel naphtha is converted to a mixture of methane, carbon dioxide, hydrogen, and a small amount of carbon monoxide in the presence of a catalyst.

The gases leaving this reactor are at a temperature of about 900°F. From the reactor they enter the methanation section of the plant where the methane content in the gas is increased. Methanation is accomplished in two stages. After the first stage, a slipstream is diverted as the feed for the hydrogen generation unit. The main stream is routed to the second stage methanation, preheated, and reacted to convert the remaining hydrogen and carbon monoxide to methane. Gas leaving this final convertor contains for the most part a mixture of methane and carbon dioxide. Table 3.4-2 shows the composition of the gas as it leaves the CRG unit and the two methanators.

TABLE 3.4-2

PLANT GAS COMPOSITIONS

Process Stage:		Out CRG	Out 1st Methanator	Out 2nd Methanator
Gas Composition mole percent	CH_4	61.2	74.8	79.0
	H_2	17.0	4.6	1.0
	CO	1.0	0.2	<0.1
	CO_2	20.8	20.4	19.9

The remaining processes in the module are concerned with upgrading the SNG by the removal of CO_2 and water vapor. The CO_2 is removed in a Benfield unit which utilizes a hot potassium carbonate aqueous wash in a packed tower. This solution is regenerated through the use of steam in a CO_2 stripper, The carbon dioxide released in the stripper is vented to the atmosphere.

Before the gas is delivered to the battery limits the water content of the gas is reduced to the required value of about 6 pounds per million scf of gas in a drying unit. The dehydration system employed in this module is a glycol unit. The wet gas is contacted countercurrently with a 99.9% triethylene glycol solution in a packed column. The glycol absorbs the water present in the SNG providing a dry product meeting sales specifications.

After passing through the CO_2 and water removal units, the following composition for the SNG is obtained:

CH_4	-	98.05% (mole)
H_2	-	1.45
CO	-	<0.10
CO_2	-	.50

Module Flow Rates

Naphtha is fed to this module at the rate of 27,245 bbls per day. This amount satisfies both the feed and fuel requirements of the plant. Assuming the module is 92% thermally efficient, 2,180 bbls per day of naphtha is consumed as fuel in the plant (BA-230).

Thus, 25,065 bbls per day of naphtha enter the hydrotreater for sulfur removal. From the HDS unit the vaporized naphtha is gasified and methanated. From the second stage methanator, 155 MM scfd of gas is produced. Of this gas, 19.9 percent is CO_2 which must be reduced to a final concentration of 0.5 percent. Thus, the Benfield CO_2 removal unit vents approximately 30 MM scfd of CO_2. The final product of 125 million standard cubic feet per day of SNG enters the dehydration unit for reduction of water vapor to pipeline specifications. The small amount of water removed from the gas stream is vented to the atmosphere, while the SNG is transmitted off-site to sales.

Module Heat Requirements

Overall module heat requirements are determined from the required amount of steam, the utility requirements of the CO_2 and H_2O removal units, and the fuel demand of the process heaters. Public Service Electric and Gas Company (LO-095) reports that exothermic reactions in the gasifier and methanators produce enough heat to supply 60% of the plant's process steam requirements. The remaining steam requirement is supplied by combusting naphtha in steam boilers. The fuel burned in the two preheaters and one superheater is also naphtha. Assuming that the fuel requirements of the module are supplied entirely by naphtha and that 40% of the steam requirement for the process is generated by naphtha combustion in the steam boilers, the

SNG module fuel consumption is 2,180 bpd. The heat requirements for the process units are presented in Table 3.4-3.

3.4.3 Module Emissions

Air emission sources within the synthetic natural gas module include (1) the flue gases from the naphtha fuel combustion in the two preheaters, the superheater, the steam boiler, the Benfield CO_2 removal system, and the glycol dehydration unit, (2) the methane released with the CO_2 that is vented from the Benfield system, (3) hydrocarbon emissions from the naphtha storage tanks, and (4) miscellaneous fugitive hydrocarbon emission sources. A summary of module air emissions is presented in Table 3.4-4.

The emissions from the fuel combustion sources are calculated using factors derived from the 1973 edition of the EPA emission factor book (EN-071). Since no factors are presented for naphtha combustion, the average between the natural gas emission factors and the distillate fuel oil emission factors (compared on a Btu basis) are used. These factors are presented in Table 3.4-5.

Besides fuel combustion emissions from the glycol dehydration unit, some glycol (considered triethylene glycol) is emitted at the water vapor vent on the glycol regenerator. These losses are estimated to be 0.1 gallons of glycol per MM scf of gas dehydrated (PR-052), of which half is vented to the atmosphere. For this module, about 30 lbs per day of triethylene glycol is vented to the atmosphere. This emission rate is reported as a hydrocarbon loss from the module.

TABLE 3.4-3

MODULE HEAT REQUIREMENT

Basis: 125 MM scfd of SNG produced

Unit	Heat Requirement Per MM scfd Output (M Btu/MM scfd)	Unit Heat Requirement (Btu/day)
HDS Preheater	4.00×10^3	5.0×10^8
Superheater & Methanator Preheater	37.87×10^3	47.3×10^8
Boiler	36.68×10^3	45.8×10^8
Benfield CO_2 Removal	24.00×10^3	30.0×10^8
Glycol Dehydration	1.00×10^3	1.3×10^8
Hydrogen Generation Unit Heater	1.22×10^3	1.6×10^8
		130.6×10^8

TABLE 3.4-4
MODULE ATMOSPHERIC EMISSIONS
(lbs/day)

Process	Particulates	SO_2	NO_x	HC	CO
HDS Preheater	17.9	7.7	197.5	6.1	11.0
Hydrogen Generation Unit Heater	5.7	2.5	100.5	2.0	3.6
Superheater and 2nd Stage Methanator Preheater	169.5	73.2	1,870.0	57.8	104.0
Steam Boiler	164.1	70.9	1,810.7	56.1	101.0
Glycol Unit	4.7	2.0	51.4	1.6	2.9
Benfield System	107.5	46.4	1,186.0	9,340*	6.6
Naphtha Storage	-	-	-	403.2	-
Fugitive Hydrocarbon Losses	-	-	-	6,375.0	-
TOTAL	469.4	202.7	5,216.1	16,241.8	229.1

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*Includes 9300 lb/day methane loss from CO_2 vent.

TABLE 3.4-5

MODULE FUEL COMBUSTION EMISSION FACTORS

Pollutant	Emission Factors ($lb/10^3$ gal)
Particulates	4.4
SO_2	1.9
NO_x	48.5*
HC	1.5
CO	2.7

---

*A NO_x factor of 72.8 $lb/10^3$ gal is used for the hydrogen generation heater because of the higher combustion temperatures (RA-119).

Public Service Electric and Gas Company (LO-095) reports that their Harrison SNG plant with a gasification capacity of 20 mm scfd releases approximately 270 tons per year of methane from the Benfield CO_2 removal system. The specific point of emission is the CO_2 vent from the top of the potassium carbonate regenerator. Therefore, for the 125 mm scfd capacity of this module, approximately 1,700 tons per year or 9,300 pounds per day of methane is emitted.

Another source of hydrocarbon emissions is the naphtha storage tanks located on the plant site. These floating roof tanks will have a total capacity of 800,000 barrels of naphtha (one-month plant requirement). The emissions are estimated using the supplement to the 1973 EPA emission factor book on hydrocarbon losses from floating roof tanks (EN-071). The factor for naphtha jet fuel is used since its Reid vapor pressure is close to that of naphtha. This factor is 0.012 lb/day-10^3 gal.

The final source of air emissions from this module is from fugitive hydrocarbon losses. These miscellaneous leaks result from process leaks at pump seals, valve stems, and flanges. Although these emissions may become significant, particularly in a facility where plant maintenance is not given sufficient attention, it is difficult to quantify these types of emissions. As a rough estimate, 0.1 weight percent of the incoming feed is considered lost as a fugitive emission (RA-119).

Liquid Effluents

The boiler make-up feedwater for the plant is first passed through an ion exchange resin unit for demineralization. Regeneration of this demineralization unit with acid and caustic wash water streams is one of the plant's liquid effluent streams.

Other sources of liquid wastes are the plant cooling system and boiler blowdown streams and waste solution from the Benfield system. These streams are discharged into holding ponds on the plant site where the water is evaporated. Since no liquid leaves the plant boundaries, the module wastewater effluent is considered to be zero.

Solid Wastes

There are no daily discharges of solid wastes from an SNG plant gasifying naphtha. Disposal of spent, inert catalysts occur periodically but are believed to pose no environmental problems.

3.5 Comparison of Module Emissions

In the previous subsections the emission rates are related to the specific module charge capacity. This approach is used in order to present the emission impact of a typical size plant for the specific industry and hence facilitate its environmental assessment for each technology. In this subsection all of the modules are adjusted to a 10^{12} Btu/day output of primary product. This adjustment is made in order to present the different module emissions on a common basis and provide a convenient comparison of the emission impact of the various technologies. This comparison is presented in Table 3.5-1. The large hydrocarbon emissions that result from these modules are primarily a result of fugitive losses (assumed 0.1 wt% of throughput).

TABLE 3.5-1

COMPARISON OF MODULE EMISSIONS

Basis: 10^{12}Btu/Day Output Primary Fuels

EMISSIONS AND EFFLUENTS	FUEL OIL[1] REFINERY	GASOLINE[1] REFINERY	PEAK-SHAVING[3] LNG PLANT	BASE LOAD[3] LNG PLANT	SNG PLANT[2]
Air Emissions (lb/day)					
Particulates	6,720	12,300	5,900	2,350	3,750
SO_x	17,000	26,800	790	11,200	1,620
CO	1,280	2,680	5,600	2,540	2,310
NO_x	12,600	35,340	75,800	82,460	41,800
HC	78,700	90,600	4,700	43,200	130,000
Water Effluents (lb/day)					
Suspended Solids	266	295	0	0	0
Dissolved Solids	9,850	10,900	0	0	0
Organic Material	56	62	0	0	negligible
Solid Wastes (lb/day)	8,500	16,500	0	0	0

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[1] Primary fuels for the refinery modules are considered to be the gasoline and middle distillate or light fuel oil product streams. The total heating values of these product streams (gasoline: 5.248x10^6 Btu/bbl, middle distillate: 5.7x10^6Btu/bbl, light fuel oil: 5.825x10^6Btu/bbl) are combined and adjusted to a 10^{12} Btu/day output basis.

[2] Pipeline quality (1000 Btu/SCF) synthesis gas is considered to be the primary fuel from the SNG plant.

[3] Primary fuel from the LNG facility is regasified liquefied natural gas (1000 Btu/SCF).

4.0 MONITORING TECHNOLOGY

Monitoring is normally divided into two categories, source and ambient. Source monitoring typically involves measuring both the concentration and flow rate in an exit stream to determine the total amount of a particular species emitted. Ambient monitoring generally involves measurement of the concentration of a species at a remote point where it has been diluted by mixing.

Monitoring may be either continuous or intermittent. Ambient monitoring is generally performed on a continuous basis since the regulations are written in terms of the maximum allowable average concentration over a particular time interval and since the dilution of a species depends on mixing conditions which are difficult to predict with any certainty. Without continuous monitoring, there is little assurance that the maximum levels actually are detected.

In source monitoring, the concentrations do not vary so widely or so rapidly, and maximums may sometimes be predicted as a consequence of changes in operating parameters (such as fuels). Regulations often are expressed in terms of allowable emissions as a function of weight or heat content of the feedstock. Because of this, source monitoring has tended to be of the intermittent type in the past, although continuous source monitoring is now required for some pollutant species in some industries.

Whether ambient or source, monitoring methods can be divided into several categories. These include manual laboratory methods, automated laboratory methods, manual field methods, and automated field methods.

The impetus for monitoring is normally provided through a requirement to demonstrate compliance with federal and/or state regulations. For many species these regulations include both source and ambient limits.

Most regulations designate a particular analysis procedure as the standard or "reference" method for a given species. These reference procedures have tended to be of the manual laboratory type since this type of analysis has historically provided the greatest confidence level in the results. This is probably because the basic standards in this type work are normally chemicals of reliable purity whereas the standards used in manual or automatic field methods are often derived from a reference gas which may be questionable because its concentration is dependent on certain temperatures or flow rates in a calibration unit. Field methods do have the advantage that they provide real time analysis whereas laboratory methods require the collection of a sample which must then be stabilized or preserved in some manner to keep it from changing in composition during transport to the laboratory.

Refineries, LNG plants, and SNG plants will all produce certain emissions as has been discussed in earlier sections. The spectrum of emissions is greatest from refineries because of the raw nature of the feedstocks and because of the wide variety of processes which may occur. The natural gas feedstock to LNG liquefaction plants is normally quite clean compared to crude petroleum. It is purified even more prior to liquefaction (thus producing some emissions), so that the feedstock to the regasification plant is very clean. SNG plants using crude oil as a feedstock could conceivable have as broad a spectrum of emissions as refineries; however, as was discussed in Section 2.3, it is unlikely that any SNG plant in this country will use crude oil as a feedstock. This discussion will thus assume a light naphtha feedstock. Since light naphtha is derived from refineries, it can be seen that emissions from SNG plants will be more limited than those from refineries.

Since the emissions from refineries should include those from SNG plants and LNG plants, refineries will be taken as a representative case for the purposes of monitoring requirements. As discussed earlier most monitoring requirements are the result of state or Federal regulations, although in some cases source monitoring may be used as an input to control of operating parameters. Monitoring requirements will be divided into ambient air monitoring, source air monitoring, and source water monitoring, all as applicable to petroleum refineries. For each category a brief review of the Federal regulatory framework will be presented, along with a discussion of monitoring methods. A discussion of solid waste disposal site monitoring is also provided.

4.1 Ambient Air Quality Monitoring

4.1.1 Background

For ambient air quality, Federal regulations have established certain criteria pollutants, namely, nitrogen dioxide (NO_2), sulfur dioxide (SO_2), carbon monoxide (CO), photochemical oxidants (O_3), particulates, and non-methane hydrocarbons (NMHC). Both primary standards (to safeguard human health) and secondary standards (to prevent damage to clothes, buildings, plants, animals, etc.) have been established. The averaging time varies for different species, with short term averages generally expressed as "not to be exceeded more than once per year". The actual regulations are quite lengthy, and are described in the Federal Register, Volume 36, No. 228, page 22384 and later modified slightly in Federal Register, Volume 38, No. 178, page 25678.

A summary is provided in Table 4.1-1. It should be noted that all measurements are to be corrected to reference conditions of 25°C and 760 mm Hg.

The various states have established their own ambient air quality regulations, and in many cases they have different averaging periods and/or more stringent limits than Federal regulations. Due to their wide variety these will not be considered here, but it is noteworthy for the purposes of monitoring around a refinery that many include regulations on hydrogen sulfide (H_2S).

In addition to specifying limits on the criteria pollutants, the Federal government has also established reference methods for their analysis. These procedures for particulates, total oxidants, nitrogen dioxide, and sulfur dioxide are outlined in Federal Register, Volume 36, No. 84, Part II, April 30, 1971. For non-methane hydrocarbons, the procedure is defined in Federal Register, Volume 36, No. 228, page 22394. Because some of these procedures are inconvenient for continuous field monitoring, and because many other types of analyzers are presently being used for field monitoring, certain mechanisms have been defined whereby other analysis procedures may be designated as reference or equivalent methods. These mechanisms are outlined in Federal Register, Volume 40, No. 33, page 7042, 1975. Because many types of instruments are currently under evaluation as reference or equivalent methods, it is not possible at this time to specify which monitoring methods will be acceptable.

4.1.2 General Monitoring Considerations

One of the most difficult areas in ambient air monitoring is the siting of the various monitors. This is especially true when the purpose of the monitoring is to evaluate the impact of a particular source. This is typically done based on dispersion

TABLE 4.1-1

SUMMARY OF FEDERAL AMBIENT AIR STANDARDS

All numbers in micrograms/cubic meter ($\mu g/m^3$)

Pollutant	Averaging Time	Primary Standard	Secondary Standard
SO_2	Annual	80	-
	24 hour*	365	-
	3 hour*	-	1,300
Particulate	Annual	75	60
	24 hour*	260	150
CO	8 hour*	10,000	10,000
	1 hour*	40,000	40,000
Total Oxidant	1 hour*	160	160
Non-Methane HC (6-9 AM)	3 hour*	160	160
NO_2	Annual	100	100

*Not to be exceeded more than once per year.

modeling which utilizes historical meteorological data plus data regarding the source to predict the location of maximum pollutant concentrations for annual and short term averages. The Environmental Protection Agency has recently undertaken several studies on optimum siting criteria for several pollutants.

For the reference procedures defined in the Federal Register, the accuracy of the analysis is given, and it is expected that any new reference or equivalent methods will be of equal or greater accuracy. For SO_2 analysis by the reference method, the relative standard deviation at the 95 percent confidence level is 4.6 percent. For total oxidants the accuracy is given as ±7 percent. For carbon monoxide an accuracy of ±1 percent of full scale is given (full scale normally is 58 milligrams per cubic meter). The accuracy of particulate analysis is given as ±50 percent, and for non-methane hydrocarbons the accuracy is 2 percent of full scale.

Costs are difficult to assess on a per sample basis for continuous analysis. Instrument costs are in the following ranges; however, multicomponent analyzers may be even higher.

Pollutant	Thousands of Dollars
SO_2	4-8
NO_2	4-8
Ozone	3-5
NMHC	5-10
CO	3-10
Particulates	0.5-15

In some cases a calibration unit costing several thousand dollars may be required to accomplish a multi-point calibration. In addition, some type of temperature-controlled shelter is required, as is a data recording system. Finally, processing the data will require manpower and/or additional hardware. It can be seen that actual monitoring costs will depend on availability of facilities and manpower, and will be different in almost every case. Many companies now offer an ambient air monitoring service in which they assume total responsibility for all instrument operation and data processing, and provide a summary report to the client on a regular basis.

The most commonly used nitrogen oxide monitors employ the chemiluminescent technique. This method is specific for nitric oxide, so nitrogen dioxide must be converted to nitric oxide prior to its analysis. By obtaining a nitric oxide measurement with and without conversion of nitrogen dioxide, the nitrogen dioxide concentration can be obtained by difference. Other popular methods for measuring nitrogen oxides include electrochemical analyzers, second derivative spectroscopy, bubblers and colorimetric analyzers, and membrane-electrochemical analyzers (IN-056).

Sulfur dioxide and hydrogen sulfide are most commonly measured with flame photometric analyzers. These detectors actually respond to the total sulfur content of a molecule, therefore, selectivity scrubbers are installed on the inlet to remove all sulfur species but the one of interest. Other analysis methods for SO_2 include electrochemical analyzers (membrane and non-membrane), pulsed fluorescent analyzers, second derivative spectroscopy analyzers, and colorimetry (IN-056). SO_2, H_2S, COS, CS_2, and other sulfur species can be measured with gas chromatographic analyzers using flame photometric detectors.

The most commonly used method for continuous ozone analysis is the chemiluminescent technique, in which ozone is reacted with ethylene or in some cases with Rhodamine-B. Other methods include ultraviolet absorption, electrochemical analyzers, second derivative spectroscopic analyzers, and wet chemistry bubblers.

Carbon monoxide is normally measured with either infrared analyzers or gas chromatographs which convert the CO to CH_4 and measure it via a flame ionization detector. Electrochemical analyzers for CO also are available.

Hydrocarbons are most commonly measured using chromatographic separation of the methane, detection via a flame ionization detector, and determination of non-methane hydrocarbons as the difference between total hydrocarbons and methane (IN-056). Continuous analyzers are now available which separate the hydrocarbons into methane, ethylene, acetylene, and total hydrocarbons. To obtain a more detailed analysis, a manually operated gas chromatographic system or gas chromatograph - mass spectroscopy combination is required. This may be achieved by collecting bag samples and taking them to the laboratory, or by installing an instrument in a field site. Continuous analysis of this sort is difficult since some concentration of the sample is normally required.

Aldehydes and organic acids are detected by the flame ionization detectors in regular environmental chromatographs. In the results, however, they are lumped into the non-methane hydrocarbons. These species can be detected using bag samples and laboratory chromatographs or with pulse polarographs.

Continuous ammonia analyzers are available based on an electrochemical principle.

Particulates are most commonly determined using the EPA High Volume sampler. A weighed filter is exposed to a measured flow of air for 24 hours, then reweighed. Average particulate mass per unit volume for the 24 hour period is obtained. Other samplers based on mass measurement using beta particles have become available in recent years. These systems can be programmed to measure for much shorter time periods than 24 hours.

Samples collected with particulate analyzers can be subjected to a detailed analysis for content of various trace elements. The most popular methods for trace element analysis are x-ray fluorescence, atomic absorption, spark source mass spectrometer, and neutron activation analysis.

4.2 Source Monitoring (Air)

4.2.1 Background

As was the case with ambient monitoring, the Federal government has established regulations for source monitoring; however, these have been on an industry by industry basis, and are for new sources. Many states have also established emission regulations, but the variety of these is too great and changes too rapid to be covered here.

For the purpose of source monitoring at a petroleum refinery the relevant regulations cover emissions from fluid catalytic cracking unit catalyst regenerators, fluid catalytic cracking unit incinerator-waste heat boilers, fuel gas combustion devices, and storage vessels for petroleum liquids (see Standards of Performance for New Stationary Sources, Federal Register, Volume 39, No. 47, page 9308, 1974). It is noteworthy that these regulations define petroleum as the crude oil removed from the earth and the oils derived from tar sands, shale, and coal. The regulations establish emission limits for particulates (both mass and opacity limits), carbon monoxide (as concentration by volume in the exhaust gas), and sulfur dioxide (as H_2S concentration in the fuel gas).

Monitoring, calibration, and reporting procedures are also specified in the same article of the Federal Register. For the purposes of determining compliance with the emission limits, certain EPA methods are specified:

Method 1 - Sample and Velocity Traverses for Stationary Sources

Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate

Method 3 - Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight

Method 4 - Determination of Moisture in Stack Gases

Method 5 - Determination of Particulate Emissions from Stationary Sources

Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources

Method 7 - Determination of Nitrogen Oxides Emissions from Stationary Sources

Method 8 - Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources

Method 9 - Visual Determination of the Opacity of Emissions from Stationary Sources

Method 10- Determination of Carbon Monoxide Emissions from Stationary Sources

Method 11- Determination of Hydrogen Sulfide Emissions from Stationary Sources

Methods 1 through 9 are described in Federal Register, Volume 36, No. 247, pages 24882-24895. Methods 10 and 11 are described in Federal Register, Volume 39, No. 47, pages 9319-9323.

These reference methods for determining compliance are generally non-continuous, manual methods. However, continuous monitors are also required for opacity and carbon monoxide measurements on the fluid catalytic cracking unit catalyst regenerator, hydrogen sulfide in fuel gases, and sulfur dioxide in exhaust streams from fuel gas combustors. The specific form of the continuous analyzers is not defined in the Standards of Performance for Petroleum Refineries.

This problem is addressed in a more recent publication, Stationary Sources, Proposed Emission Monitoring and Performance Testing Requirements, Federal Register, Volume 39, No. 177, page 32852. It should be noted that these are proposed rules, not promulgated standards. Probably the most significant aspect of these proposed rules is that no "product line certification" is given whereby certain instrument specifications (measurement method, response time, etc.) would be provided for each pollutant, and any instrument meeting these specifications could be installed on a specific source in fulfillment of the monitoring requirements for that source. Instead, certain performance specifications are defined, and it is left to the owner or operator of each source to demonstrate that the continuous monitoring system he has selected meets those performance specifications on his source. Detailed procedures and forms are provided for demonstrating agreement with the performance specifications for opacity, nitrogen oxides, sulfur dioxide, and oxygen. Performance specifications for systems which monitor hydrogen sulfide and carbon monoxide are to be proposed at a later date.

These same proposed rules include a modification to EPA Method 9 for the visual determination of opacity of emissions from stationary sources. Special exceptions are provided for those who have already installed continuous analyzers since the first standards were promulgated on December 23, 1971.

4.2.2 General Monitoring Procedures

Generally speaking, accurate source monitoring is more difficult than ambient monitoring. The gas streams typically are hot, difficult to access, and the pollutant concentrations may vary as a function of position in the exit stack. Introduction of standard gases in a meaningful manner often is difficult.

As with ambient monitoring, source monitoring may be intermittent or continuous, manual or automated. In addition, continuous monitors can be divided into in-situ and external systems. The external monitors normally require a sample conditioning system.

As discussed earlier, the reference methods tend to be of the intermittent manual type. Because of sampling difficulties these tend to be somewhat more expensive than ambient monitoring. As an example, it has been estimated by EPA that one particulate analysis using Method 5 will cost from $3,000 to $10,000 depending on the source, including some 300 man-hours of effort (Federal Register, Volume 39, No. 47, page 9309). A single ambient particulate measurement using a high-volume sampler costs only a small fraction of this amount. The Federal Register does not list measurement accuracies for Methods 1-11.

The same general instrument types are used for continuous source monitoring as for ambient monitoring. Pollutant concentrations in stack gases are normally several orders of magnitude higher than ambient levels so that the instruments must either be designed for higher levels or dilution systems must be used. For external monitors, a sample conditioning system often is required to provide an air sample suitable for analysis. This involves filtering out particulates (unless particulates are being monitored), removing excess water, and providing for introduction of calibration gases.

Because sample conditioning systems increase cost and complexity, and may decrease reliability, several in-situ monitors have been developed. In these systems the detection or measurement portion is mounted directly in the exit stack. As with the external monitors, however, calibration is often difficult. An excellent discussion of external analyzers, in-situ analyzers, and remote sensors has been provided by Nader (NA-113).

Nitrogen oxides are commonly measured with chemiluminescent analyzers, infrared analyzers, or ultraviolet analyzers. Sulfur dioxide is measured with ultraviolet analyzers, flame photometric analyzers, infrared analyzers, or pulsed-fluorescence analyzers. Carbon monoxide is most commonly measured with infrared analyzers. Continuous particulate analyzers utilize the beta particle detector.

4.3 Effluent Water Monitoring

4.3.1 Background

Based on the Federal Water Pollution Control Act, the Federal government has established guidelines and standards for the Petroleum Refining Point Source Category (see Federal Register, Volume 39, No. 91, page 16560, 1974). Standards are established for the following subcategories:

Topping Subcategory
Cracking Subcategory
Petrochemical Subcategory
Lube Subcategory
Integrated Subcategory

These standards include both existing and new sources, and are sub-divided according to the following groups:

1) Effluent limitation guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPCTCA)

2) Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BATEA)

3) Standards of performance for new sources

4) Pretreatment standards for new sources

Exceptions to the limits prescribed for the BPCTCA group may be obtainable from the EPA Regional Administrator in certain cases.

Limits are listed in terms of maximum for any one day and average of daily values for thirty consecutive days, and the units are expressed as kilograms per thousand cubic meters of feedstock. The specified limits in each group are scaled according to size factors and process configurations for individual plants. (Proposed amendments to the guidelines are provided in Federal Register, Vol. 39, No. 202, page 37069, 1974.) The species for which limits have been set include the following:

BOD5
TSS
COD
Oil and grease
Phenolic compounds
Ammonia as N
Sulfide
Total Chromium
Hexavalent Chromium
pH

Total organic carbon (TOC) limits are set for runoff water and once through cooling water. Also, in some cases, TOC may be substituted for COD if the effluent contains more than 1000 milligrams per liter of chloride.

EPA has established test procedures for the analysis of many pollutants, including those listed above (see Federal Register, Volume 38, No. 199, page 28758, 1973). These procedures are contained in the document "Methods of Chemical Analysis of Water and Wastes", U.S. Environmental Protection Agency, EPA report 625-/6-74-003, 1974. For each species, an analysis method is described including sampling and preservation techniques, the required apparatus, and the precision and accuracy.

Analysis costs are dependent on the required number of analyses of each type. Assuming only one analysis of each type, however, commercial water analysis laboratories will normally charge prices in the range of those in Table 4.3-1.

It should be noted that the Petroleum Refining Point Source Category briefly addresses solid waste control. No definite regulations or limits are established; however, recommendations for choice of landfill sites and for record keeping regarding these sites are presented.

4.3.2 General Water Monitoring

Automated analyzers for water analysis have been available for many years for both field and laboratory applications.

TABLE 4.3-1

WATER ANALYSIS COSTS

BOD_5	\$10 - 15
TSS	5 - 7
COD	10 - 15
Oil and Grease	10 - 15
Phenolics	15 - 20
Ammonia	10 - 15
Sulfide	8 - 12
Total Chromium	3 - 5
Hexavalent Chromium	5 - 8
pH	1

The species normally measured in the field are temperature, pH, conductivity, and dissolved oxygen; however, recent developments in membrane electrodes have greatly expanded the parameters which can be detected.

Automated laboratory analyzers are very useful when large numbers of similar samples are to be analyzed; however, for a few samples the set-up time largely negates the automatic analysis feature.

The general situation regarding laboratory versus field and manual versus automated samplers has been well summarized by Phillips and Mark (PH-019). Table 4.3-2 provides a summary of their results.

It can be seen that automated field analyzers are available for many of the species for which effluent limitations have been established for petroleum refineries. These include total organic carbon, chemical oxygen demand, ammonia, and chromium. Of course pH monitors are also available. Automated laboratory analyzers can be used for analysis of phenolics and sulfide.

Other metals besides chromium could be analyzed for if desired. Manual or automated laboratory analyzers using the atomic absorption method or neutron activation method can detect many metals down to the sub-parts per billion level. Both soluble species and solid species (present in the suspended solids) can be examined.

Analysis for specific hydrocarbon species normally requires a gas chromatograph for separation plus some form of detector. Combining a mass spectrograph with the gas chromato-

TABLE 4.3-2

TYPICAL INSTRUMENTAL METHODS

Instrument Method	Pollutant Measured
Manual Laboratory Analyzers	
Atomic absorption	Metals
Colorimetric	Metals; nutrients (ammonia, nitrate, nitrite, phosphate) chemical oxygen demand; total organic carbon
Emission spectrometry	Metals; phosphorus
Gas chromatography	Pesticides
Gas membrane electrodes	Dissolved oxygen; ammonia, nitrite; BOD
Ion selective electrode	Nitrate
Activation analysis	Metals; nitrogen; phosphorus
X-ray fluorescence	Metals
Gas chromatography/ Mass spectrometry	Pesticides
Thin-layer chromatography	Pesticides
Infrared spectrophotometry	Total organic carbon
Automated Laboratory Analyzers	
Atomic absorption	Metals
Colorimetric	Metals; nutrients
Gas chromatography	Pesticides
Manual Field Monitors	
Colorimetric	Metals; nitrite; phosphate
Electrode	DO; metals
Volumetric titration	DO; nitrate
Automated Field Monitors	
Atomic absorption	Hg
Colorimetric	Cr; MnO_4^-; $PO_4^=$; Fe; Cu; NH_3; NO_3^-; NO_2^-; total phosphorus; chemical oxygen demand
Electrometric	Cu; dissolved oxygen; NH_3; NO_2^-
Flame ionization; infrared	Total organic carbon

graph provides a particularly powerful tool for hydrocarbon studies, although analysis of this sort becomes quite expensive.

For the measurement of aldehydes, manual polarographic and gas chromatographic techniques are available.

4.4 Solid Waste

Refinery solid wastes are normally either incinerated or disposed of in a landfill. In the case of incineration, the problem reverts to the air monitoring situation. Landfill disposal is normally regulated on a state or local basis, if at all. The principles set forth in EPA's "Land Disposal of Solid Waste Guidelines" (40 CFR, Part 241) may be used as guidance for acceptable land disposal techniques, however.

Solid waste disposal from refineries is briefly addressed in Petroleum Refining Point Source Category Effluent Guidelines and Standards, Federal Register, Volume 39, No. 91, page 16563, 1974. This section points out that best practical control technology and best available control technology as they are known today require disposal of the pollutants removed from waste waters in the form of solid wastes and liquid concentrates. Whether these wastes contain hazardous metals or organic species is not well established. Caution thus dictates that landfill sites be selected to prevent horizontal or vertical transport of species from the landfill into groundwater or surface waters. When this is not accomplished by the natural geologic conditions, adequate liners should be provided. It is recommended that permanent records be kept as to the location and nature of the disposal sites.

Monitoring requirements for landfills in general and those for refinery wastes specifically have not been well established. The problem is basically viewed as one where soluble species dissolve in water percolating through the landfill, and are transported into nearby groundwater aquifers. The identity and solubility of the species in the landfill thus are important, but both of these can change with time in the complex chemical and bacterial environment of the landfill. To further complicate matters, soluble species transported out of the landfill area may subsequently be removed via interaction with soil particles.

A series of monitoring wells can be installed around a landfill to monitor any changes in groundwater quality. Such a network must be very carefully designed, however, as groundwater movement often is quite slow. Considerable contamination can occur before it is detected, and it is almost impossible to remove all the contamination once it reaches the aquifer.

5.0 EMISSION CONTROL METHODS

In this section emission control techniques are examined for the air, water, and solids emissions resulting from the refinery, LNG, and SNG modules. Both currently available control methods and potential control techniques are considered. Due to the similarity in emissions and emission sources and the fact that LNG and SNG processes may be considered as one process or subset of petroleum processing, the refinery, LNG, and SNG technologies are considered together rather than individually. Control technologies are considered in relation to the specific emission, i.e., particulate, hydrocarbon, CO, etc., and the specific source or application. Controls are discussed for gaseous, liquid, and solid wastes.

5.1 Air Emission Control

As established in Section 3.0 of this study, the major air emissions from the refinery, SNG, and LNG industries contain particulates, sulfur oxides, carbon monoxide, nitrogen oxides, and hydrocarbons. The current technology and practices used in the control of these emissions are addressed in this section.

5.1.1 Particulates Emission Control

The major source of particulates from the LNG, SNG, and refinery modules are process heaters, boilers, incinerators, and the fluidized catalytic cracking unit (FCCU) catalyst regenerator in the gasoline refinery operation. The particulates from the process heaters and the boilers result from ash within the fuel oil, naphtha, or fuel gas combusted. Presently, there is no incentive for particulate controls on these types of process heaters and boilers, due to the low concentration of particulates in the flue gas. There is presently no proposed Federal Standard for particulate concentrations in flue gases from process heaters used in refining, LNG, or SNG plants.

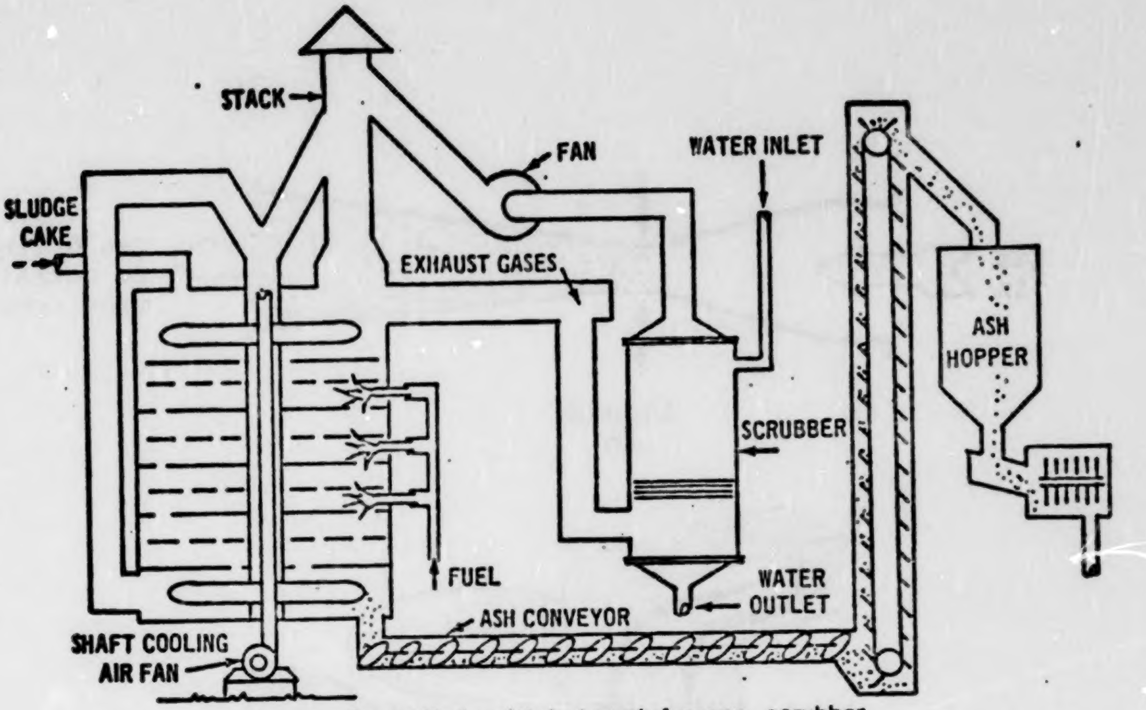
5.1.1.1 Sludge Incineration Particulate Control

The proposed particulate emission standard from the EPA for sludge incineration is 0.031 gr/dscf (EN-072). These particulates primarily result from fly ash in the incinerated sludge. Average uncontrolled particulate emissions are 0.9 grain/dscf for a multiple-hearth incinerator and 8.0 grain/dscf for a fluidized bed incinerator (EN-072). In order to meet the proposed standard, particulate removal efficiencies of 96.6%

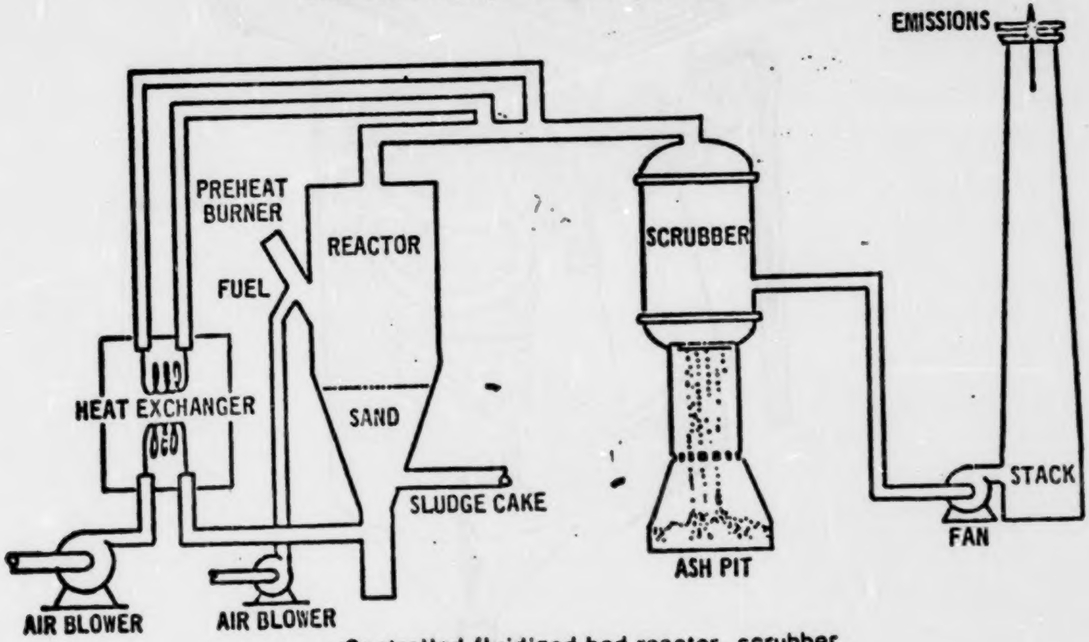
for a multiple-hearth incinerator and 99.6% for a fluidized bed are required. Flow diagrams for the controlled multiple-hearth furnace and the controlled fluidized bed reactor are given in Figure 5.1-1.

Typical particulate control for sludge incinerators is by a venturi scrubber or an impingment-type scrubber (EN-072). With a venturi scrubber (Figure 5.1-2), water which is fed through jets in a venturi section is suspended as water droplets. The fly ash collects on the suspended water droplets and is removed along with the water in a cyclone. An impingement scrubber (Figure 5.1-3) works on much the same principle. Fly ash laden gas is blown upward through a series of perforated plates which are covered with a stream of water. The gas atomizes the water and the water spray droplets collect the fly ash. The fly ash and water are again removed by a cyclone. Overall efficiencies for a single plate range from 90 to 98% for 1 micron particles or larger (NA-029). The advantage of the impingement method is a lower pressure drop through the scrubber. An alternate method for particulate removal would be bag or fabric filters (Figure 5.1-4). Bag filters will give removal efficiencies of greater than 99%; however, the bag filters are generally more expensive to install and operate (NA-029). Electrostatic precipitators are another alternative; however, they too are more expensive than wet scrubbing (NA-029). An approximate monetary comparison is given in Table 5.1-1.

Disposal of incinerable sludge by methods that do not involve the use of incineration are most desirable from the air pollution standpoint. In many cases these alternative


STACK
FAN
WATER INLET
SLUDGE CAKE
EXHAUST GASES
ASH HOPPER
SCRUBBER
FUEL
WATER OUTLET
ASH CONVEYOR
SHAFT COOLING AIR FAN

Controlled multiple-hearth furnace, scrubber.


EMISSIONS
PREHEAT BURNER
REACTOR
SCRUBBER
FUEL
HEAT EXCHANGER
SAND
SLUDGE CAKE
STACK
FAN
ASH PIT
AIR BLOWER
AIR BLOWER

Controlled fluidized bed reactor, scrubber.

FIGURE 5.1-1 INCINERATOR EMISSIONS CONTROLS
SOURCE: (EN-072)

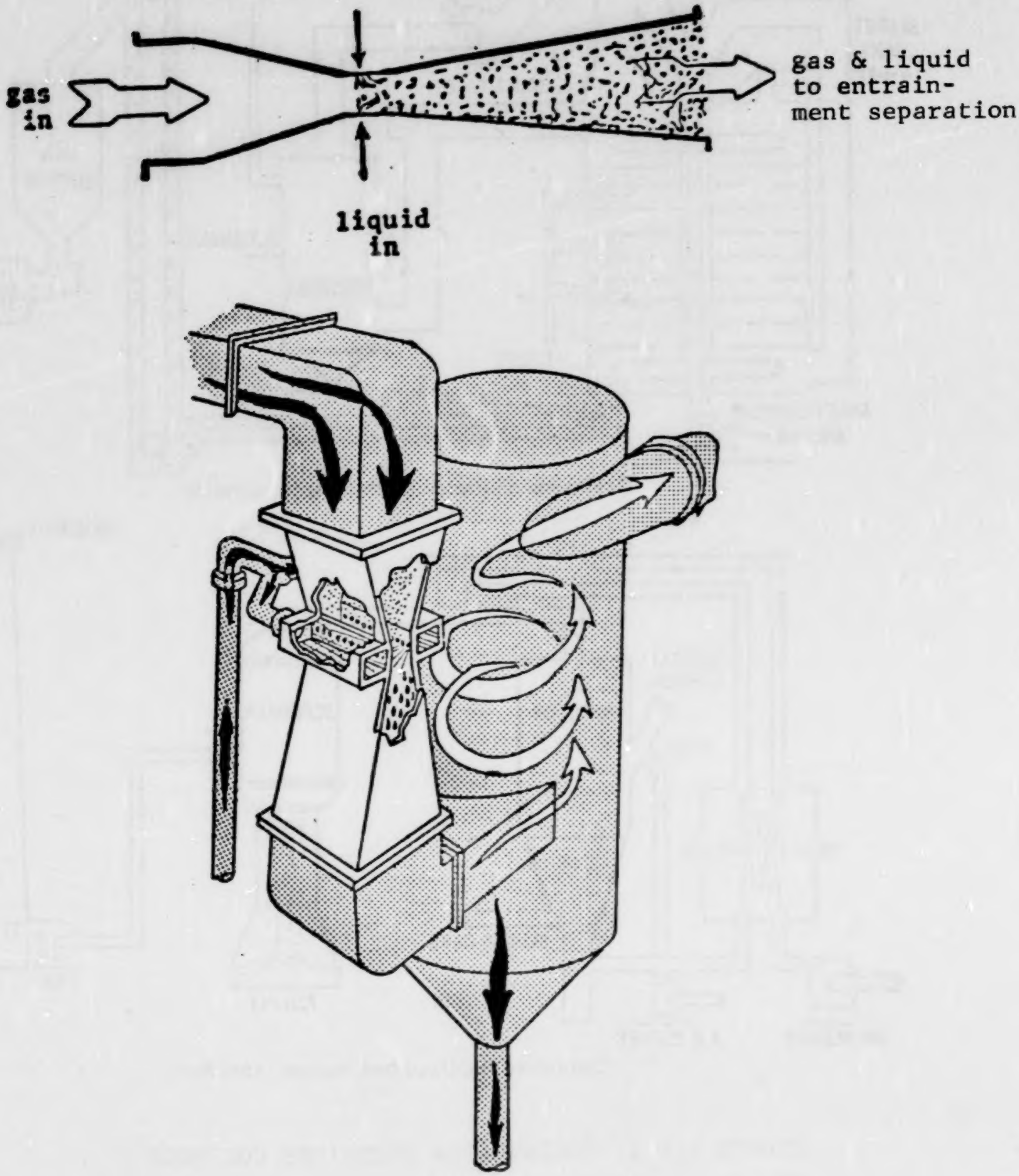

gas in
liquid in
gas & liquid to entrainment separation

FIGURE 5.1-2 VENTURI SCRUBBER

SOURCE: (NA-029)

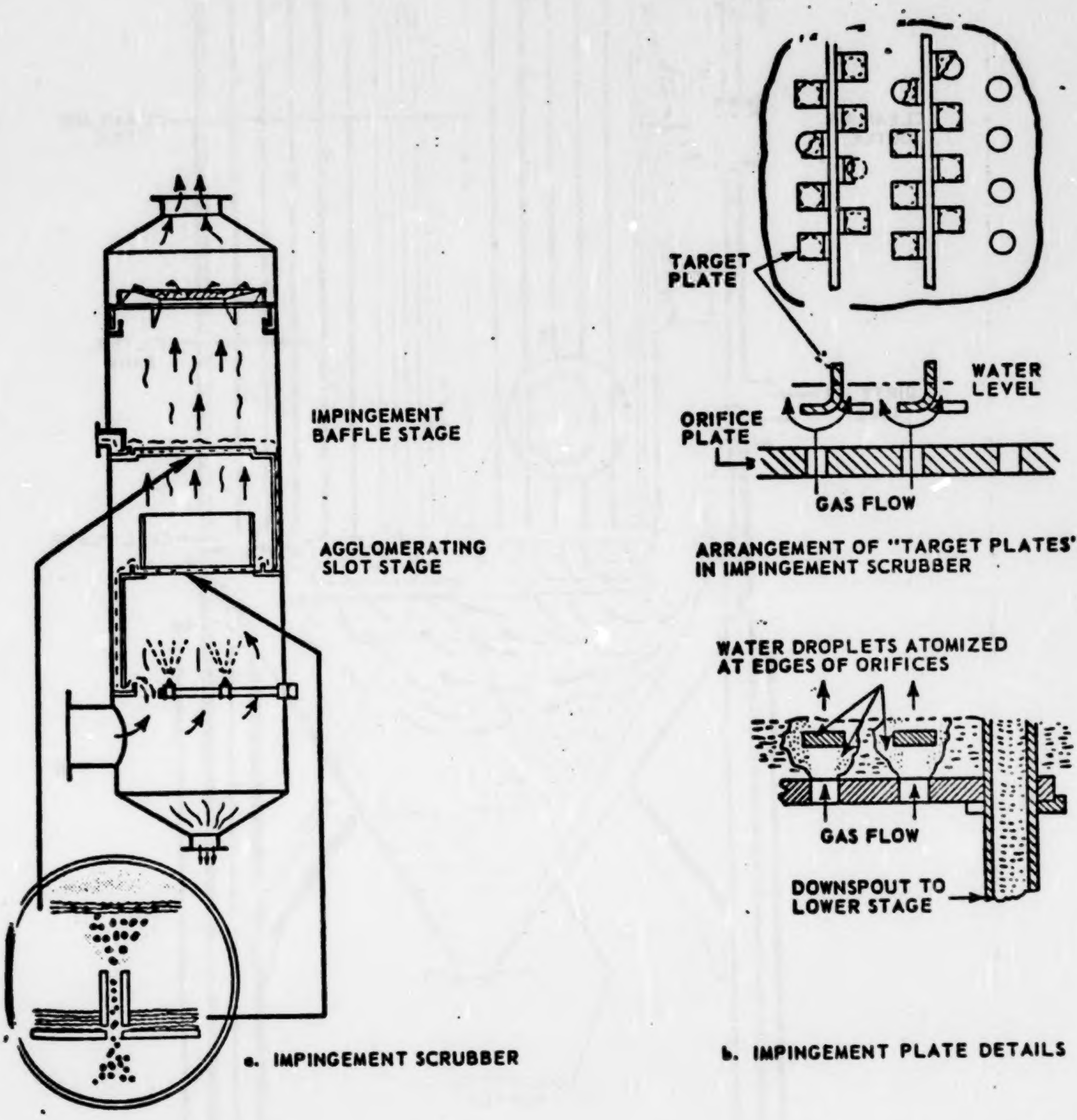

IMPINGEMENT BAFFLE STAGE
AGGLOMERATING SLOT STAGE
a. IMPINGEMENT SCRUBBER
TARGET PLATE
WATER LEVEL
ORIFICE PLATE
GAS FLOW
ARRANGEMENT OF "TARGET PLATES" IN IMPINGEMENT SCRUBBER
WATER DROPLETS ATOMIZED AT EDGES OF ORIFICES
GAS FLOW
DOWNSPOUT TO LOWER STAGE
b. IMPINGEMENT PLATE DETAILS

FIGURE 5.1-3 IMPINGEMENT PLATE SCRUBBER
SOURCE: (NA-029)

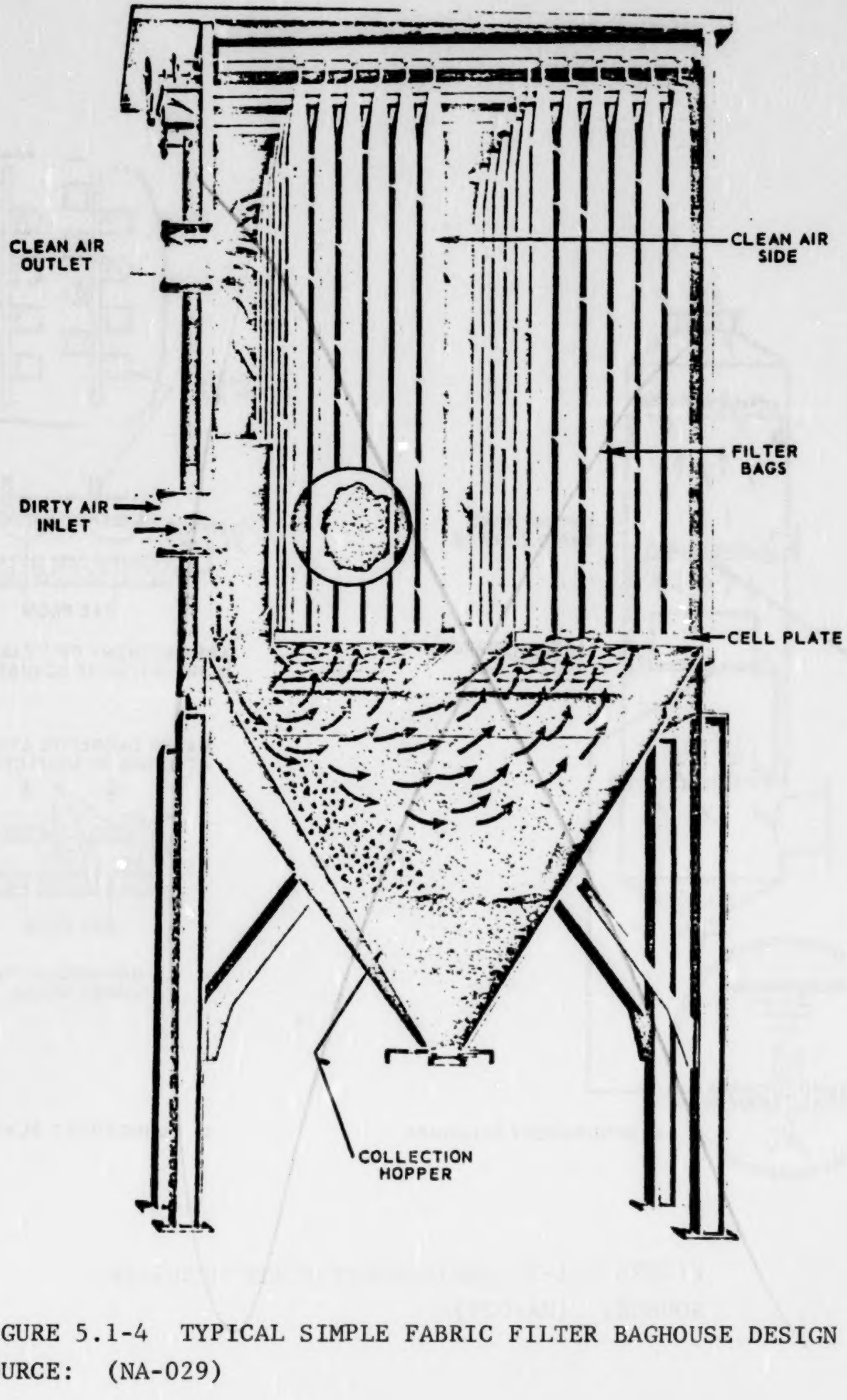

CLEAN AIR
OUTLET
CLEAN AIR
SIDE
FILTER
BAGS
DIRTY AIR
INLET
CELL PLATE
COLLECTION
HOPPER

FIGURE 5.1-4 TYPICAL SIMPLE FABRIC FILTER BAGHOUSE DESIGN
SOURCE: (NA-029)

FIGURE 5.1-4

TYPICAL SIMPLE FABRIC FILTER BAGHOUSE DESIGN

SOURCE: (NA-029)

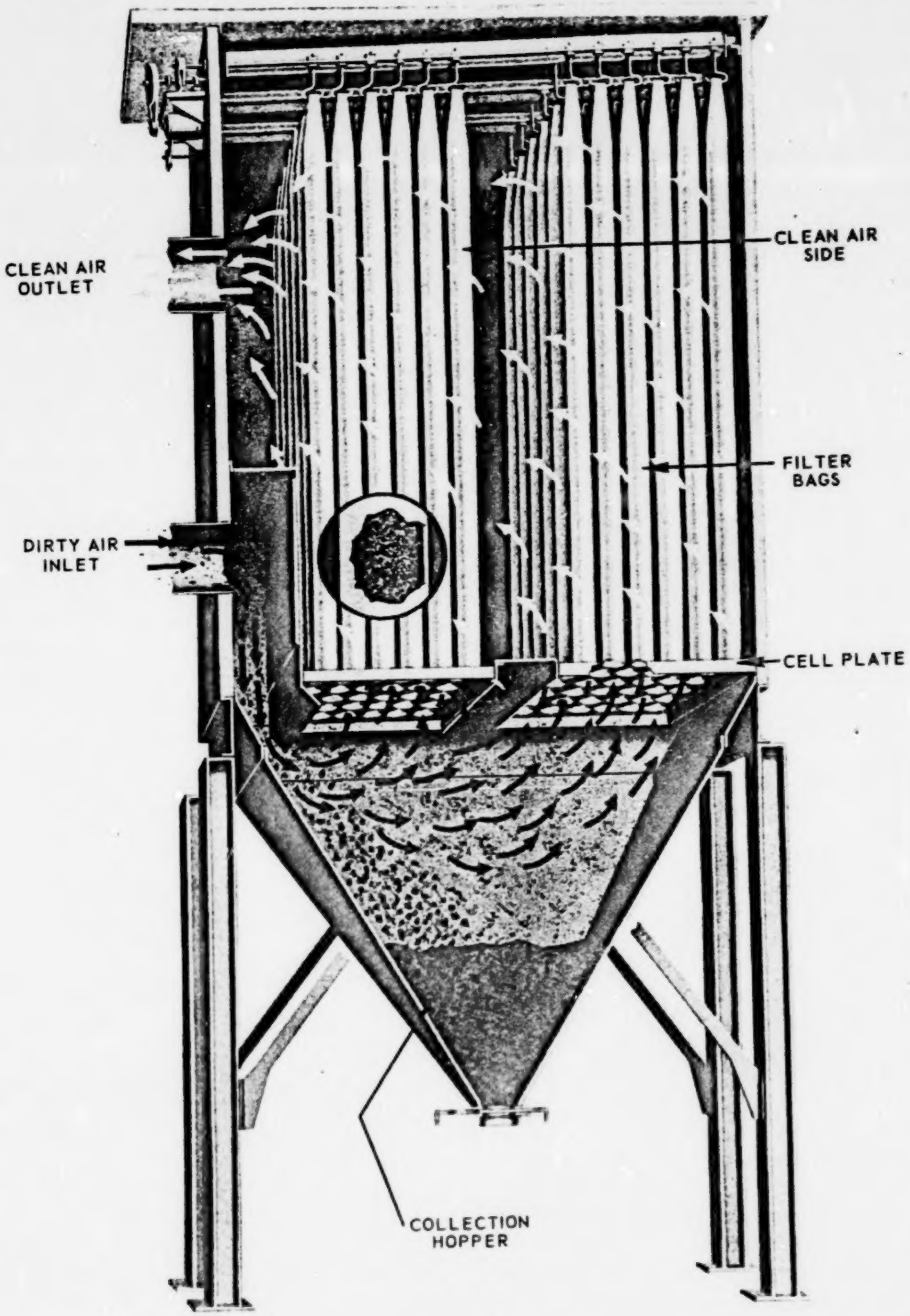

CLEAN AIR SIDE
CLEAN AIR OUTLET
FILTER BAGS
DIRTY AIR INLET
CELL PLATE
COLLECTION HOPPER

TABLE 5.1-1

RULE-OF-THUMB COSTS OF TYPICAL COLLECTORS OF STANDARD MILD-STEEL CONSTRUCTION

(MAR 1973)

	Dollars Per Cubic Feet Per Minute		
Type of Collector	Equipment Cost	Erection Cost	Yearly Maintenance and Repair Cost
Mechanical Collector	0.07-0.25	0.03-0.12	0.005-0.02
Electrostatic Precipitator	0.25-1.00	0.12-0.50	0.01-0.025
Fabric Filter	0.35-1.25	0.25-0.50	0.02-0.08
Wet Scrubber	0.10-0.40	0.04-0.16	0.02-0.05

SOURCE: (RE-070)

methods may also prove more economical. One method for sludge removal is landfill. Air emissions from landfill are limited to diesel combustion of the hauling and compacting equipment and miscellaneous particulate emissions entrained in the air by earth-moving equipment. The miscellaneous particulates can be controlled by proper waterspraying techniques. Other alternatives are described in Section 5.3 on Solids Emission Control.

5.1.1.2 FCCU Particulate Control

The particulates from the FCCU catalyst regenerator result from catalyst fines. The proposed standard particulate level from the FCCU regenerator is 0.022 grain per scf of flue gas. Particulate emissions from the catalyst regeneration process are on the order of 0.1 to 0.2 pounds per ton of catalyst recirculated (NA-029). Based on the estimated module air flow rate of 64,000 cfm and a catalyst regeneration rate of 2,500 tons per hour, it can be calculated that the catalyst regenerator will require 98% removal of fines to meet this requirement (CU-016).

Modern-day techniques of wet scrubbing or baghouse filters are quite adequate for this type of removal, except for the fact that the flue gas exits the regenerator at a temperature too high for these control methods. Normally, a multiple cyclone type arrangement is employed for particulate control. Basically, a cyclone is a settling device in which a strong centrifugal force, acting radially, is used in place of a relatively weak gravitational force acting vertically (Figure 5.1-5). The multiple cyclone setup removes nearly all of the particles greater than 40 microns (WI-073). The gases from the cyclones are introduced into a carbon monoxide boiler where the CO is combusted to CO_2. The sensible heat of the flue gas stream and the heat of combustion of the CO are used to produce steam.

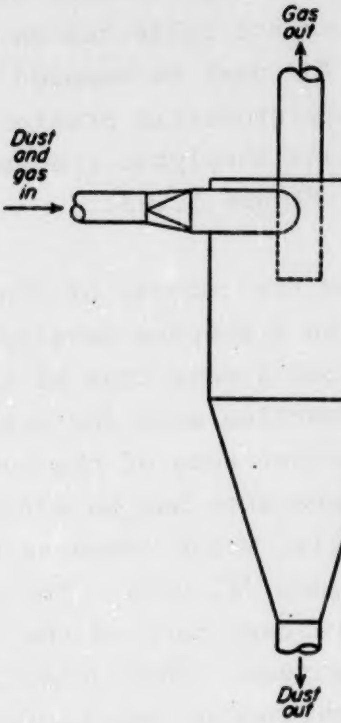

Gas out
Dust and gas in
Dust out

FIGURE 5.1-5 CYCLONE

From the CO boiler the gas is routed through an electrostatic precipitator where the remaining particulates are further reduced. The electrostatic precipitator removes particulates by charging the particles with a high-voltage direct-current corona. The charged particles are collected on a large plate-like collection electrode. The dust is removed from the electrodes by rapping or washing. An electrostatic precipitator is shown in Figure 5.1-6. Typical fluid catalytic cracker particulate control systems are shown in Figure 5.1-7.

An alternate method for removal of fines coming from the multiple cyclones would be a process developed by Shell which uses a multiple tube, swirl vane type of centrifugal separator (WI-073). In conjunction with the separator a turbo-expander is used to recover some of the power in the flue gas stream. The main separator has an efficiency of 99.5% for the 10 micron size particle, which compares to 85% for the highest efficiency large cyclone (WI-073). The centrifugal separator concentrates the greatest part of the particulate matter in a small underflow stream. This underflow stream is then cleaned by use of baghouses or wet scrubbers. A flow scheme of the Shell-type process is given in Figure 5.1-8.

A very new method for recovering catalyst fines is by the use of a granular bed filter. The granular bed filter was designed to reduce fine catalyst losses and is used in place of both the multiple cyclones and the electrostatic precipitator. The catalyst dust-laden gas is blown into a chamber containing granular sand bed filter elements. The catalyst fines are collected on the surface and in the interstices of the bed. When a predetermined resistance pressure is reached across the bed, a short pulse of high pressure air is shot in reverse flow through the filter elements. The air fluidizes the sand bed and releases the catalyst fines which are captured within the chamber. A granular bed filter is shown in Figure 5.1-9.

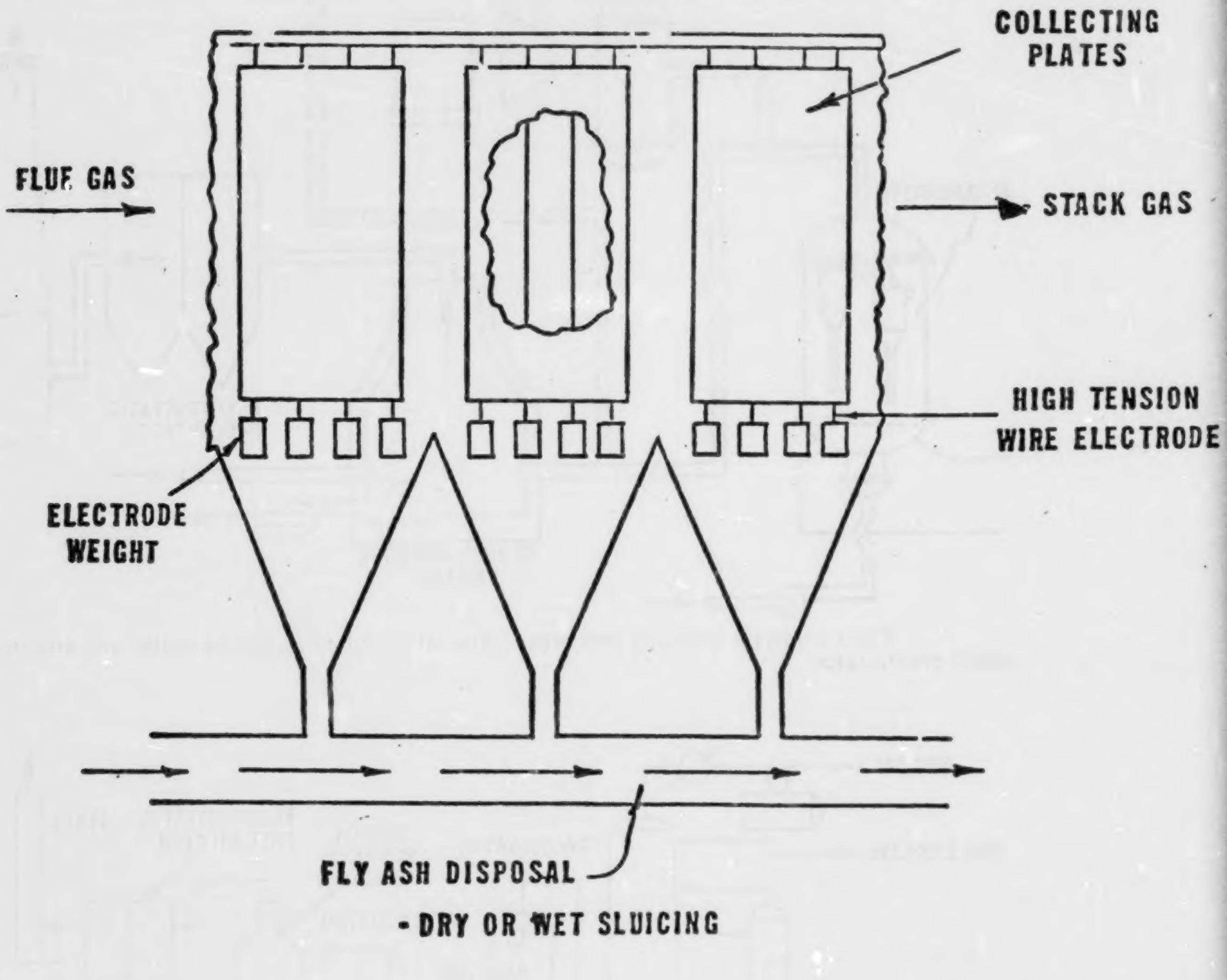
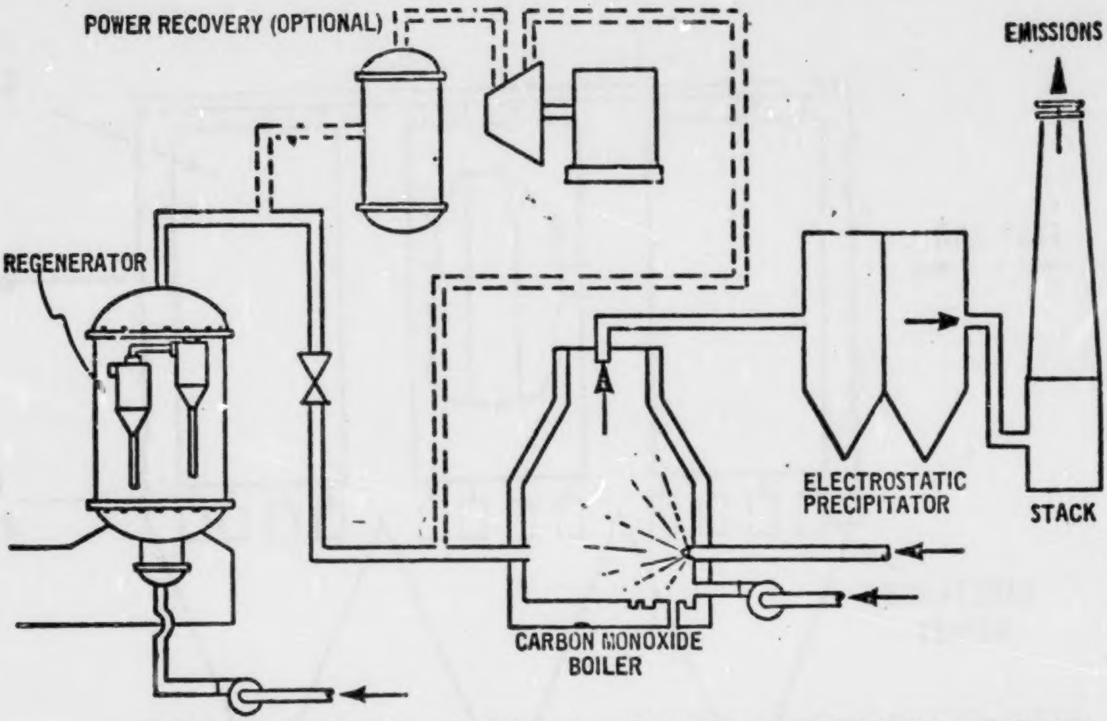
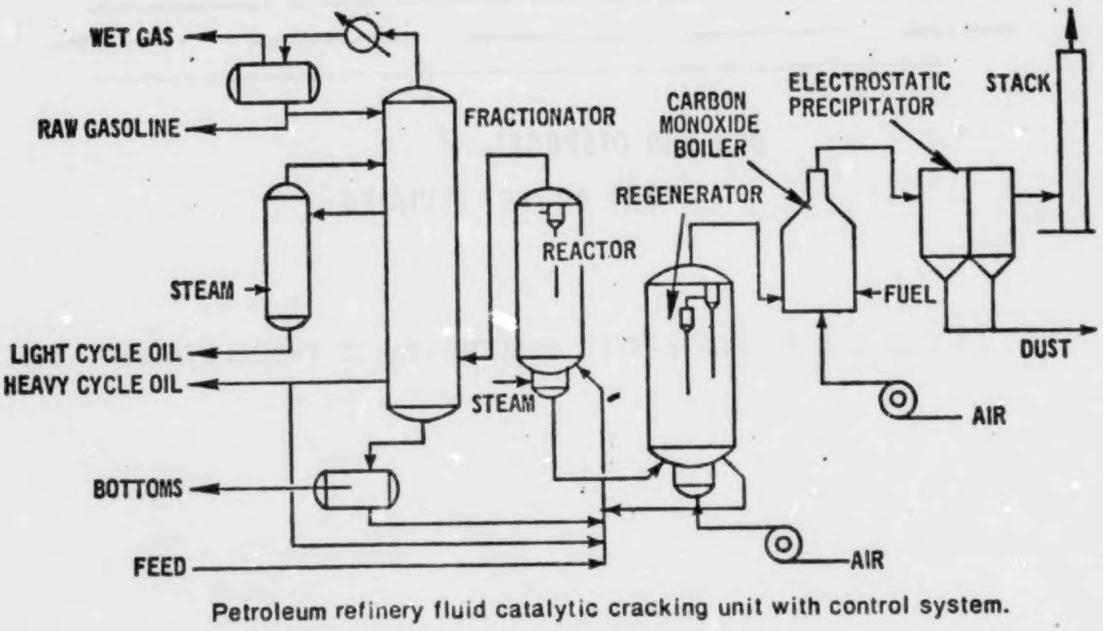

COLLECTING PLATES
FLUE GAS
STACK GAS
HIGH TENSION WIRE ELECTRODE
ELECTRODE WEIGHT
FLY ASH DISPOSAL
- DRY OR WET SLUICING

FIGURE 5.1-6 PLATE-TYPE ELECTROSTATIC PRECIPITATOR


POWER RECOVERY (OPTIONAL)
EMISSIONS
REGENERATOR
ELECTROSTATIC PRECIPITATOR
STACK
CARBON MONOXIDE BOILER

Fluid catalytic cracking unit regenerator with carbon monoxide boiler and electrostatic precipitator.


WET GAS
RAW GASOLINE
FRACTIONATOR
CARBON MONOXIDE BOILER
ELECTROSTATIC PRECIPITATOR
STACK
REGENERATOR
REACTOR
STEAM
FUEL
LIGHT CYCLE OIL
HEAVY CYCLE OIL
STEAM
DUST
AIR
BOTTOMS
FEED
AIR

Petroleum refinery fluid catalytic cracking unit with control system.

FIGURE 5.1-7 FCCU PARTICULATE CONTROL SYSTEMS

SOURCE: (NA-029)

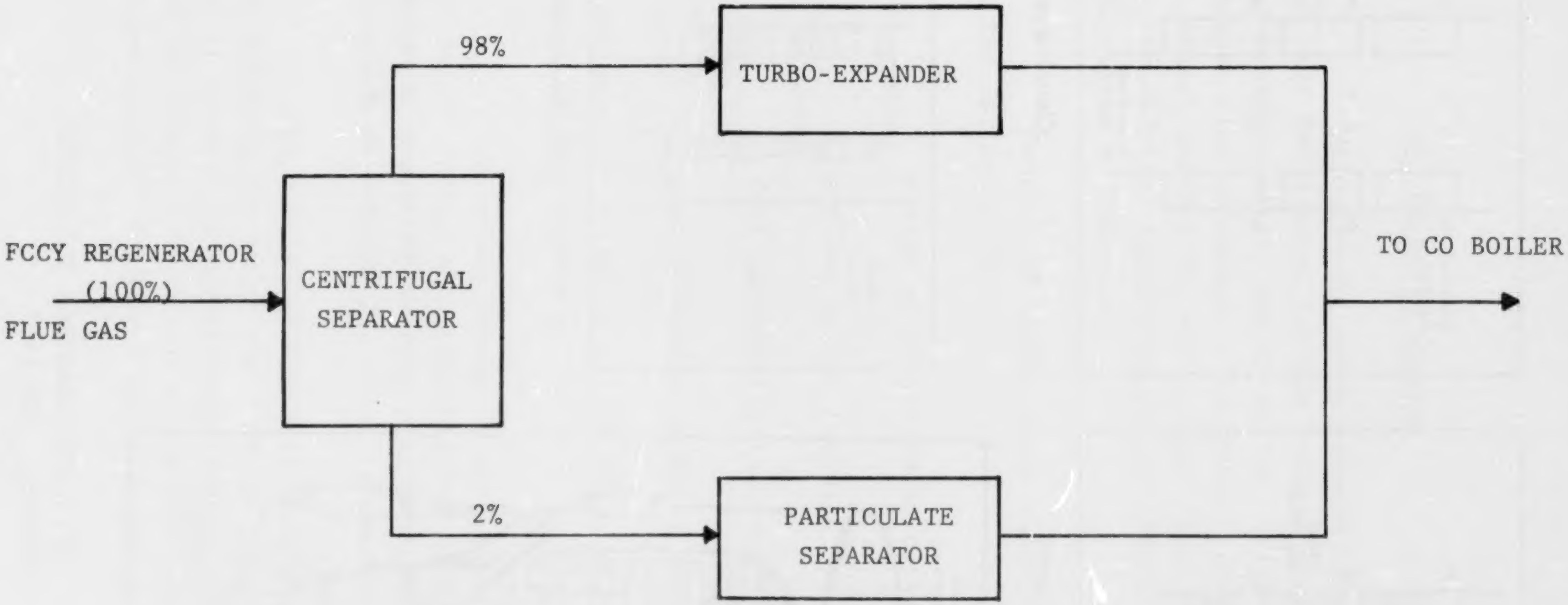
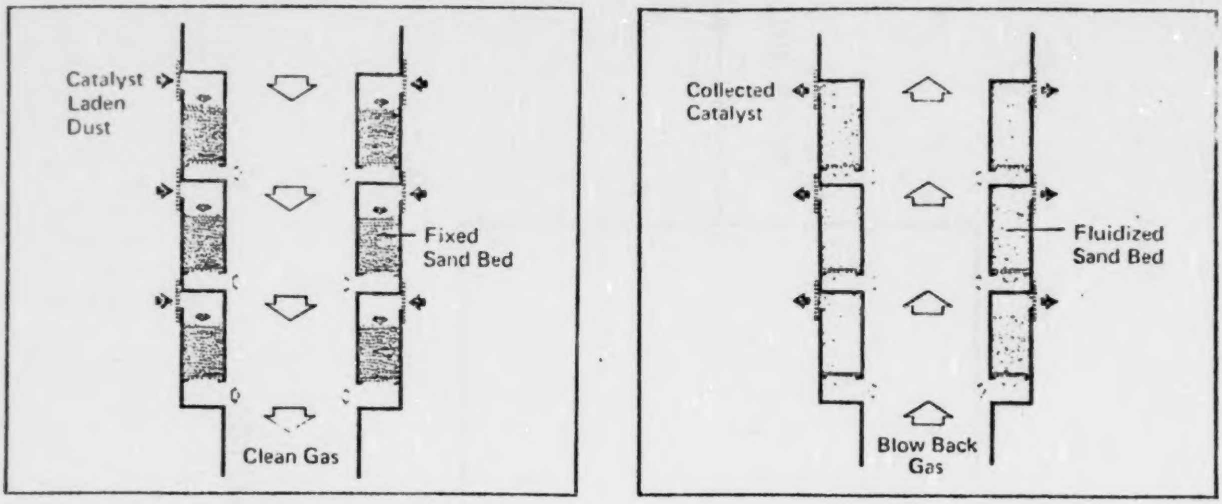
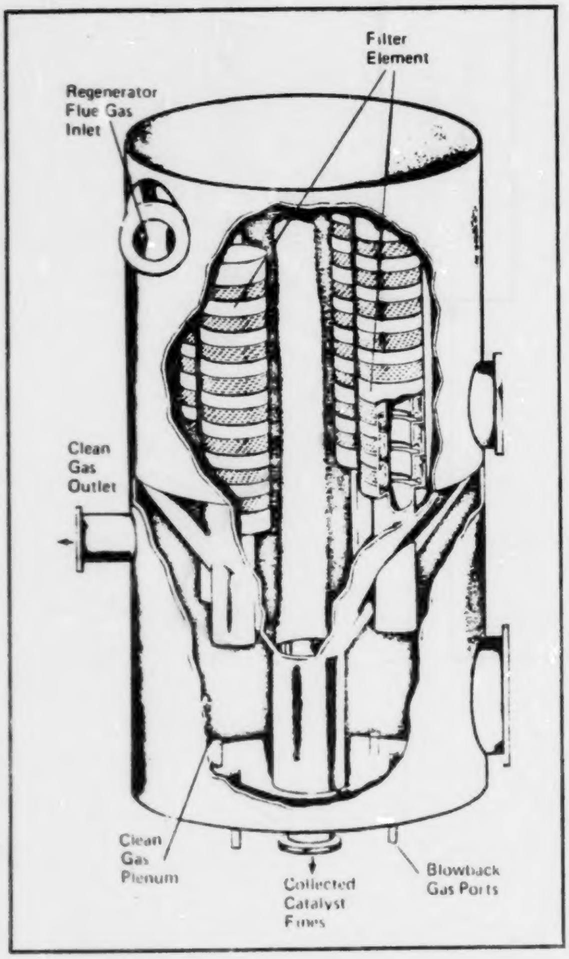

FCCY REGENERATOR
(100%)
FLUE GAS
CENTRIFUGAL SEPARATOR
98%
TURBO-EXPANDER
2%
PARTICULATE SEPARATOR
TO CO BOILER

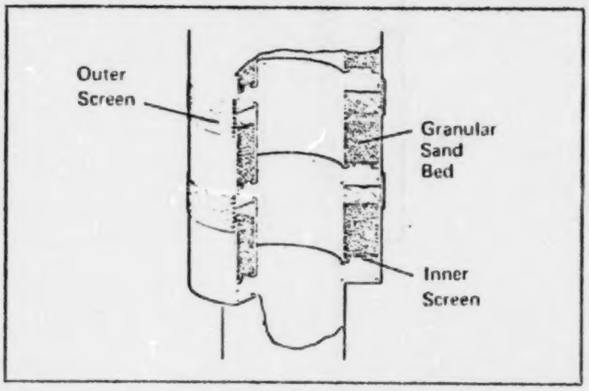
FIGURE 5.1-8 SEPARATOR - ENERGY RECOVERY SYSTEM


Catalyst Laden Dust
Fixed Sand Bed
Clean Gas
Collected Catalyst
Fluidized Sand Bed
Blow Back Gas

Operating cycle.

Cleaning cycle.


Filter Element
Regenerator Flue Gas Inlet
Clean Gas Outlet
Clean Gas Plenum
Collected Catalyst Fines
Blowback Gas Ports


Outer Screen
Granular Sand Bed
Inner Screen

Filter element internals.

(Courtesy of Ducon Co., Inc., Mineola, N. Y.)

FIGURE 5.1-9 THE DUCON GRANULAR BED FILTER
SOURCE: (KA-149)

5.1.2 SO_x Emission Control

Major sulfur oxide emission sources from the refinery, LNG, and SNG modules include process heaters, boilers, the tail gas treating plant, the CO boiler, the incinerator, and catalyst regeneration processes. The Federal government has established stringent ambient SO_x air quality levels (EL-062). Control of SO_x is of vital importance in the design of a modern refinery, LNG plant, or SNG plant.

Control of sulfur oxide emissions can be accomplished in the following ways:

- design of processes to conserve energy,
- use low sulfur fuels,
- fuel desulfurization, and
- removal sulfur products after combustion of fuel.

A combination of any or all of these techniques will reduce the amount of SO_x emissions.

Conserving energy is an obvious solution, but until the recent energy shortages had not been examined very closely. Design of new energy-saving plants and processes in the petroleum as well as all other industries is of prime importance.

Use of low sulfur fuel is also an obvious solution for reducing SO_x emissions. Natural gas is the cleanest fuel, but it is also in the shortest supply. Refineries, SNG plants, and LNG plants are in the unique position, however, where they either produce or process natural gas and thus have easy access to it. Although the price of natural gas is climbing, refineries are tending to use natural or fuel gas produced from the refining operations to fire their process heaters and thus reduce emissions.

5.1.2.1 Fuel Desulfurization

Sulfur or hydrogen sulfide are removed from fuels before firing to reduce eventual SO_x emissions to the atmosphere. The two main fuels in the refinery, SNG plant, or LNG plant are natural gas and heavy fuel oil. Natural gas as well as refinery fuel gases such as coke-gas are usually treated by an absorption process involving an aqueous, regenerative sorbent. A number of gas treating processes are available, and they are distinguished primarily by the regenerative sorbent employed. Popular sorbents are amine-based solvents, hot carbonate solutions, and various organic liquids such as N-methyl-pyrrolidone and dimethyl ether of polyethylene gycol (HY-014). Sulfur compounds may also be removed through adsorption processes by the use of molecular sieves. These absorption and adsorption processes have the additional advantage of removing CO_2 and thus increasing the heating value of the fuel gas. A typical treated natural gas stream has a H_2S concentration of 0.25 grain per scf (HY-014).

Amine-based solvents are most commonly used (NG-002). The solutions most often employed contain either monoethanolamine (MEA), diethanolamine (DEA), or triethanolamine (TEA). The amine sorbent used will depend on the properties of the sour gas. The most common amine solution is a 10 to 20% DEA solution.

A typical amine treating plant is shown in Figure 5.1-10. The "sour" gas is contacted with the amine solution in an absorber to remove H_2S. The rich amine solution is pumped to a regenerator where "acid" gas is removed from the amine sorbent.

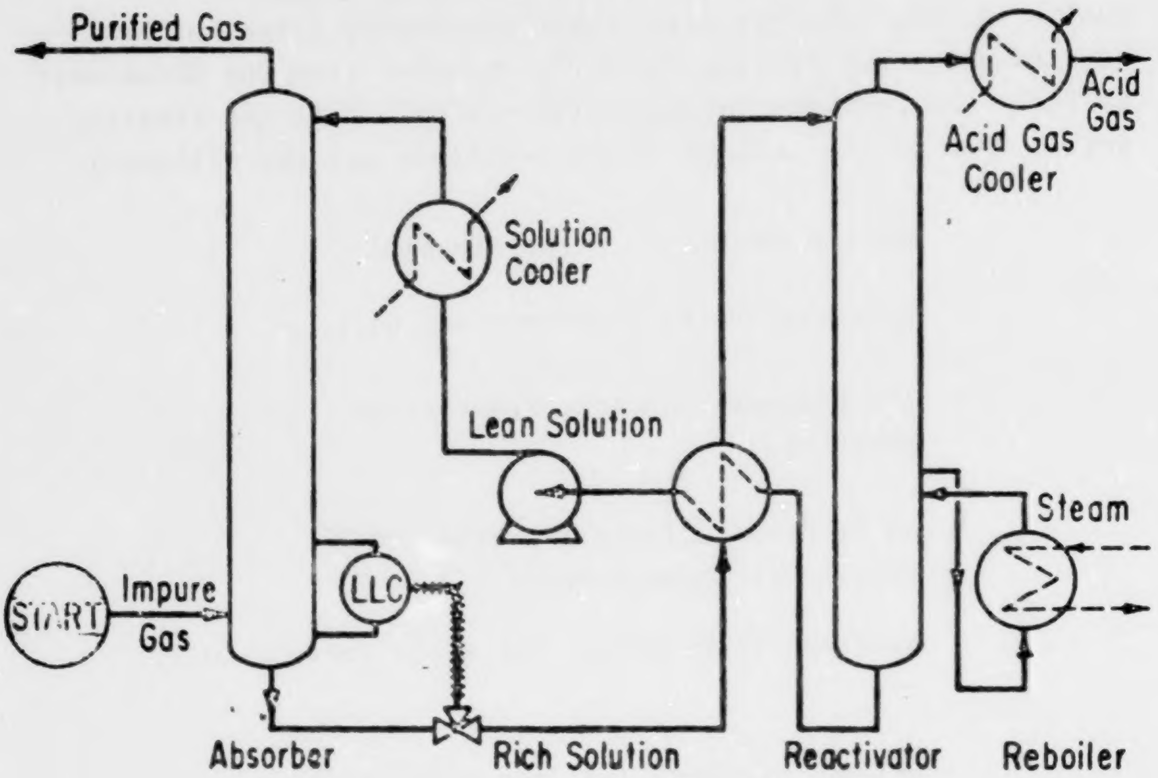

Purified Gas
Solution Cooler
Acid Gas Cooler
Acid Gas
Lean Solution
Steam
START
Impure Gas
LLC
Absorber
Rich Solution
Reactivator
Reboiler

FIGURE 5.1-10 TYPICAL GAS TREATING PROCESS UTILIZING AN AMINE SORBENT

The "acid" gas is processed through a Claus plant for recovery of sulfur compounds as elemental sulfur. Conversion efficiencies in the Claus plant up to 98% can be attained but will depend on the hydrogen sulfide concentrations in the acid gas fed to the unit, the number of catalytic stages and the quality of the catalyst used. When processing large volumes of acid gas, however, the total SO_x emission from the Claus unit is large and requires further treatment by a tail gas treating unit. Some of the tail gas units available are the following:

- Beavon (Union Oil of California),
- Cleanair (J. F. Pritchard and Co.),
- IFP Process (Institut Francais du Pétrole),
- Shell Claus Off-gas Treating - SCOT (Shell Development Co.),
- Sulfreen (SNPA/Lurgi; the R. M. Parsons Co.), and
- W-L SO_2 recovery (Wellman - Power Gas, Inc.)

All of these units will increase the Claus recovery of equivalent sulfur in the tail gas to greater than 99.5% (HY-014). The use of different units is determined by the characteristics of the tail gas, the operating conditions, and the economics of the situation.

The other major fuel used in the refinery is heavy fuel oil. Treating heavy fuel oil for sulfur removal is done by hydrodesulfurization. Processes available for hydrodesulfurization are listed in Table 5.1-2 (HY-013). Residuals treating processes which are listed usually produce a heavy fuel oil as one of the products from hydrodesulfurization. Major problems arise from inability to economically convert over 90% of the sulfur in the residual to H_2S and from metals buildup in the reactor. Heavy metals tend to poison or plug catalysts used in hydrodesulfurizing residuals which means added expense due to frequent replenishing of catalysts.

A new and rather novel method for treating residual material in a refinery is flexicoking. The flexicoking process was designed by Exxon Research and Development and is shown in Figure 5.1-11. The advantage of flexicoking is that its major product streams are lighter than the fuel oil products from resid hydrodesulfurization excluding a relatively small amount of coke product. The product streams being lighter are more efficiently treated for sulfur removal. Also, the heavy metals in the feedstock are conviently concentrated in the coke material.

Lighter fuels such as gas oil or naphtha which are also combusted in the refinery and SNG plant are readily hydrodesulfurized to a low sulfur concentration. The majority of existing processes involve reaction of sulfur in the fuel with hydrogen gas over a catalyst bed. Typical catalysts are cobalt-molybdenum, nickel-molybdenum, and nickel-tungsten (HY-013). The gas oil and naphtha sulfur content can be economically reduced to 5 ppm or less (HY-013). Sulfur oxide emissions from the fluidized catalytic cracker (and eventually the CO boiler) can be reduced by desulfurizing the gas oil feed entering the unit.

Fixed bed catalysts such as those used for hydrodesulfurization in the refinery, the SNG plant, or the LNG plant are usually replaced on an annual or biannual basis. In the past, hydrogen sulfide and sulfur/dioxide emissions from regeneration processes have been either uncontrolled or controlled by routing

TABLE 5.1-2

HYDRODESULFURIZATION PROCESSES

Process (Source)	Desulfurized Petroleum Products	Description	% Sulfur Reduction	Development Status	Developer
H-oil (HY-013, JI-008)	Heavy gas oils and residuals	Embullated bed reactor-vapor/liquid system where the catalyst is fluidized by an upward flow of liquid	88-90%	Full-scale	Cities Service Research and Development Co. and HRI
RCD Isomax (WA-073)	Heavy fuel oils	Fixed bed catalyst reactor	80-93%	Full-scale	UOP Process Div. of Universal Oil Products Co.
GO-fining (HY-013)	Heavy fuel oils	Fixed bed catalyst reactor	90%	Full-scale	Exxon Research and Engineering Co. and Union Oil Co. of California
Resid-fining (HY-013)	Residuals	Fixed bed catalyst reactor	60-90%	Full-scale	Exxon Research and Engineering Co. and Union Oil Co. of California
Gulf-HDS (HY-013)	Residuals	Fixed bed catalyst reactor operated at high pressure	90%	Full-scale	Gulf Research and Development Co.
RDS and VRDS (HY-013)	Residuals	Fixed bed catalyst reactor	80-90%	Full-scale	Chevron Research Co.
Resid Hydroprocessing (HY-013)	Residuals	Fixed bed reactor with highly selective catalyst	80-90%	Pilot Plant	Standard Oil Co. **(Indiana)**
Residue Desulfurization (GO-051)	Residuals	Fixed bed reactor with highly selective catalyst	80-90%	Full-scale	BP Trading Ltd.
IFP Hydrofining (AU-015)	Residuals	Fixed bed catalyst reactor	NA	Pilot Plant	Institut Francais du Petrole

SIMPLIFIED FLEXICOKING
FLOW PLAN

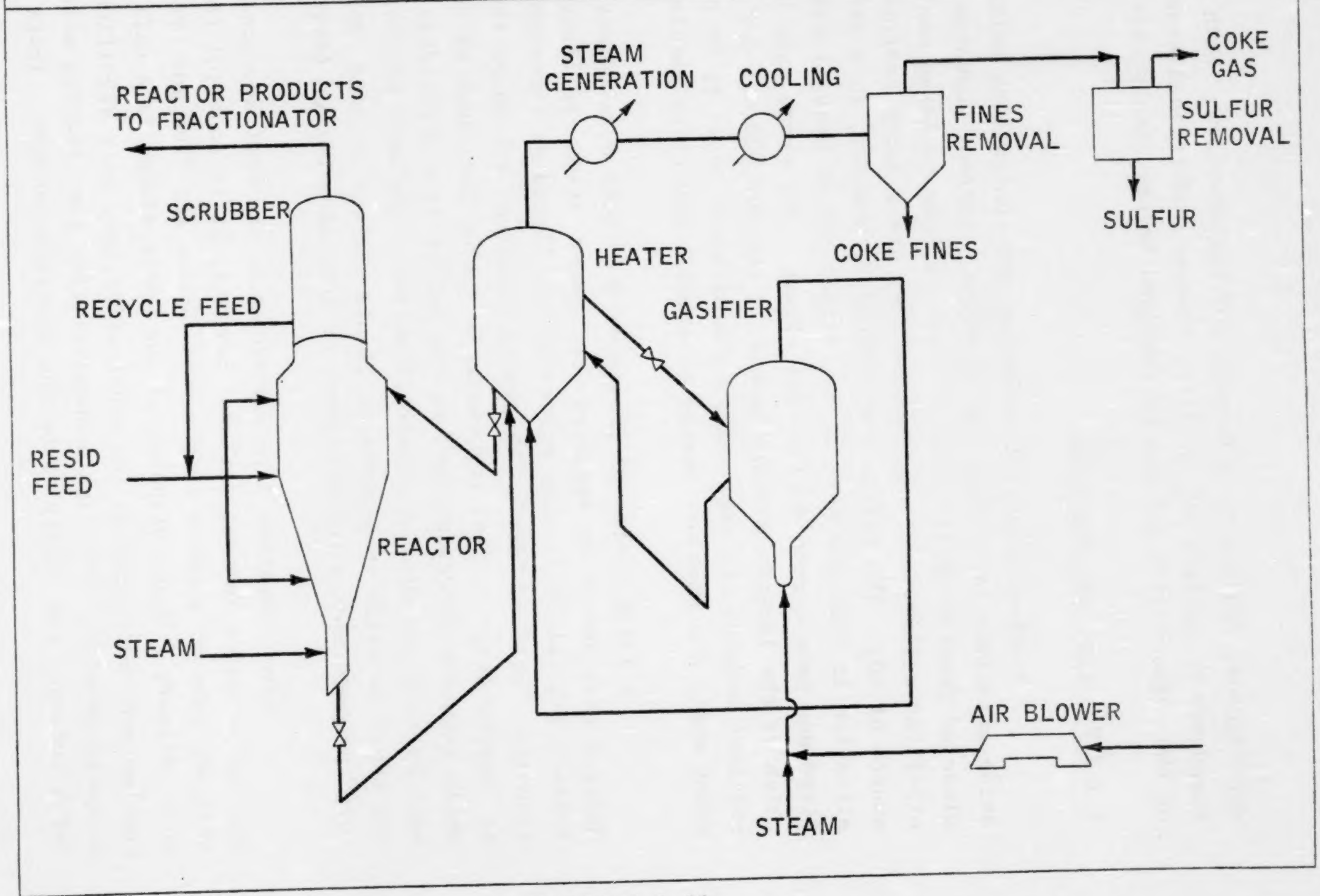

REACTOR PRODUCTS TO FRACTIONATOR
STEAM GENERATION
COOLING
COKE GAS
FINES REMOVAL
SULFUR REMOVAL
SCRUBBER
SULFUR
HEATER
COKE FINES
RECYCLE FEED
GASIFIER
RESID FEED
REACTOR
STEAM
AIR BLOWER
STEAM

FIGURE 5.1-11

Source: KE-128

the regeneration gas to a furnace for incineration. With new standards on ambient SO_x quality, however, additional treating of the regeneration gas may be required before atmospheric emission.

5.1.2.2 Flue Gas Treating

Another potential technique for controlling sulfur oxide emissions is by flue gas treating. Present research is directed towards application of these methods to large coal or oil-fired utility boilers, because they are a large emission source of SO_x. The refinery environment, however, is a different situation in that the heaters are either oil or natural gas-fired and have a much smaller gas volume. The crude unit heater, which is the largest process heater in the 200,000 bbl per day refinery modules, is approximately equivalent to an 85 Mw power plant while the smallest heater is about 1,000 times smaller.

A large number of processes are under development. Several that are at an advanced development stage are listed in Table 5.1-3 (EL-062). The processes are listed as throwaway or recovery, "wet" or "dry". Throwaway processes are where the sulfur is "thrown away" in some unmarketable sulfur form such as $CaSO_3$, while recovery processes recover the sulfur in a marketable form such as sulfuric acid or elemental sulfur. The "wet" processes are those in which an aqueous or liquid sorbent is used, while a "dry" process uses a solid sorbent or activated carbon (char) bed.

Lime-limestone type scrubbing is the most advanced of the sulfur oxide removal methods; however, it is doubtful that this SO_2 removal process is the best choice for flue gas treatment in a refinery. Waste disposal of the waste sludge is a difficult problem and, depending on the application, may be a significant economic penalty. The most economical flue gas treating methods for a refinery are likely to be the recovery methods. There are

TABLE 5.1-3

LEADING COMMERCIALLY AVAILABLE PROCESSES FOR SO_2 REMOVAL FROM FLUE GASES

Process Name	Type of Process	Comments	Sulfur Reduction	Developer	Sources
Wet Scrubbing With Limestone	Wet Throwaway	Probably the least expensive process to install.	>85%	Several Developers	EL-062 EP-009 SL-053
Wet Scrubbing With Lime	Wet Throwaway	Higher sorbent costs but increased efficiency	>90%	Several Developers	EL-062 SL-053
Double Alkali	Wet Throwaway	Smaller scrubbers and liquor flows possible.	>90%	General Motors, Combustion Equip. Assoc., Inc. and A. D. Little, Inc.	LA-142 EL-062
Magnesia Scrubbing (MGO)	Wet Throwaway	Sulfuric acid produced at central plant from $MgSO_3$ salts shipped from power plant. Regenerated MgO is returned to the scrubbing system.	90%	Chemico-Basics	SL-053 EL-062 KO-133
Catalytic Oxidation	Wet Throwaway	Catalytic oxidation occurs at 850°F. producing 80% sulfuric acid	85%	Monsanto Enviro-Chem Systems, Inc.	MI-137 EL-062
Wellman-Lord/ SO_2 Reduction	Wet Recovery	Wellman-Lord process produces concentrated SO_2 by thermal stripping of $NaHSO_3$. SO_2 may be reduced to S with natural gas.	90%	Wellman-Lord	PO-091 EL-062
Shell - CUO Catalyst Reduction	Dry Recovery	Advantages of dry scrubbing, regenerated by hydrogen, low pressure drop across absorber.	90%	Shell Development Co.	PO-109

definite reasons for this. First, many recovery processes require H_2 or H_2S as reducing agents to regenerate the sorbent and produce sulfur. Availability of these gases within the refinery (or SNG plant) makes recovery process economics much more favorable. Secondly, many recovery processes need Claus plant capacity and the refinery is normally already equipped with a Claus plant. This would mean design of a new refinery would only require a larger Claus unit to handle the acid gases from the flue gas treaters. The added sulfur production can be credited as a marketable product. Finally, if sulfuric acid is the final product such as from the catalytic oxidation process, the produced acid can be used in the alkylation process. If sulfuric acid-type alkylation is used, however, one must then contend with the problem of waste acid disposal which is another source of SO_x emissions.

One of the commercial SO_x removal processes being used as a flue gas treater in a refinery is the Shell flue gas desulfurization process (PO-109). This process uses cupric oxide as a dry, selective adsorbent to remove the SO_2. The regeneration processes releases the sulfur in the form of SO_2 which is recovered as elemental sulfur in a Claus unit. A flow diagram of the Shell unit is shown in Figure 5.1-12.

Currently, much effort is being put into development of "second generation" SO_2 scrubbing systems. Potentially applicable SO_2 scrubbers for refinery heaters and for boilers are shown in Table 5.1-4. All of these processes are currently in the pilot-plant stage of development.

Incineration of oily sludge and biological waste is also a source of SO_x in the refinery. Once again as mentioned in the section of particulates control, the best solution is to landfill the generated solids. However, if incineration is deemed necessary, stack gas cleaning processes such as just discussed could be used effectively in reducing SO_x emissions.

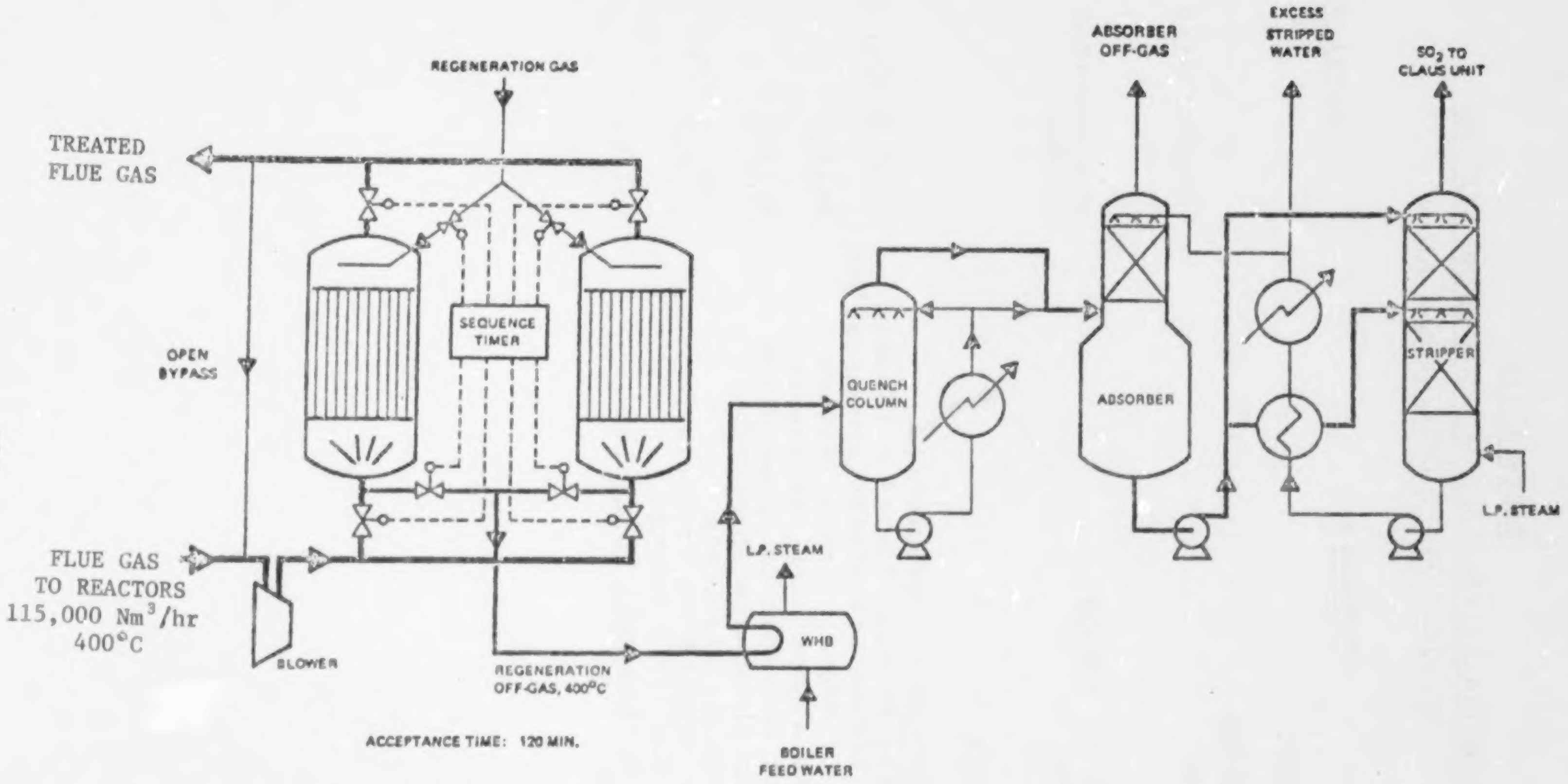

REGENERATION GAS
TREATED FLUE GAS
OPEN BYPASS
SEQUENCE TIMER
FLUE GAS TO REACTORS 115,000 Nm³/hr 400°C
BLOWER
REGENERATION OFF-GAS, 400°C
ACCEPTANCE TIME: 120 MIN.
L.P. STEAM
WHB
BOILER FEED WATER
QUENCH COLUMN
ABSORBER OFF-GAS
ABSORBER
EXCESS STRIPPED WATER
SO₂ TO CLAUS UNIT
STRIPPER
L.P. STEAM

FIGURE 5.1-12 PROCESS FLOW SCHEME OF THE SHELL FLUE GAS DESULFURIZATION SYSTEM

TABLE 5.1-4

POTENTIALLY FEASIBLE SO_2 SCRUBBING SYSTEMS IN PILOT PLANT DEVELOPMENT STAGE

Processes	Final Product
A. Dry Processes	
1. Metal Oxides	
B&W/Esso	concentrated H_2SO_4 , Sulfur
2. Carbon	
a. Bergbau Forschung	concentrated H_2SO_4
b. Westvaco	sulfur
B. Wet Processes	
Alkali Absorbents (recovery)	
a. Stone and Webster/Ionics - (Sodium absorption-electrolytic regeneration)	weak H_2SO_4, Sulfur
b. Bureau of Mines Citrate (Sodium citrate absoption-H_2 regeneration)	Sulfur
c. Stauffer Chemical Co. Powerclaus (Sodium phosphate absorption)	Sulfur
d. TVA Ammonium Bisulfate	$(NH_4)_2 SO_4$, Sulfur
e. Catalytic/Institute Francais du Petrole (IFP) Ammonia	Sulfur
f. Consolidation Coal Potassium Formate	Sulfur

5.1.3 NO_x Emission Control

NO_x emissions in the petroleum refineries, the LNG processing plant, and the SNG processing plant modules result from process heaters, boilers, the steam-naphtha reformer, incinerators, and the CO boiler which is fueled by the fluidized catalyst regenerator flue gas. The major factors determining the amount of NO_x produced are the adiabatic flame temperature within the process heater, the amount of oxygen available to combine with the nitrogen, and the length of time which N_2 and O_2 remain in high concentrations in high temperature regions (BA-230).

Nitrogen oxide and dioxide can potentially be controlled by various process techniques or modifications. The four general categories describing these techniques or modifications are the following:

1) combustion modifications to alleviate conditions favorable to NO_x formation,

2) fuel modifications, by denitrification, use of additives or the substitution of low NO_x forming fuels,

3) new or alternate designs of low NO_x forming processes, and

4) treatment of flue gases for NO_x removal.

All four of these control techniques will be reviewed in the following sections. One must, however, be careful in applying the developing technology to process heaters or small boilers since most current developments are for large utility boilers. The applicability to process heaters and small industrial boilers is largely undefined (BR-199).

5.1.3.1 Combustion Modifications

One combustion modification for reducing NO_x involves reducing the excess air used in firing the heater (JA-056). This method, however, presents a problem for small process heaters in that regulation of air flow may be quite difficult due to the varying composition and heat content of the fuel gas and fuel oil. Generally, process heaters are fired with a large excess of air to compensate for these fluctuations. This method actually does help reduce NO_x emissions in that the temperature within the heater is reduced due to the "cooling" effect of the excess air. The reduced temperature reduces NO_x formations.

A second method for NO_x reduction is two-stage combustion. In two-stage combustion, some burners are operated "fuel-rich". This is to say that the fuel is combusted with an air flow supplying only part of the stoichiometric amount of oxygen required for complete combustion. Other burners are run "air-rich" or on air only. The NO_x emissions reduction may be explained by the following factors:

1) there is a lack of oxygen available for NO_x formation in the "fuel-rich" burners,

2) the flame temperature is lower in the "fuel-rich" burner,

3) heat removed between the two stages will cause a decrease in the maximum flame temperature, and

4) the effective residence time for NO_x formation at the peak temperature is reduced (JA-056).

Two-stage combustion may, however, not be applicable to small process heaters. Excellent combustion conditions are needed for two-stage combustion to work adequately. If conditions are not favorable, flames will impinge on furnace tubes causing hot spots and caking (NA-005).

Another combustion technique for reducing NO_x emissions involves reducing the load on the heater and thus reducing the fire box temperature in the heater (JA-056). With a decreased fire box temperature, the oxygen and nitrogen will have less residence time in a high temperature environment. A disadvantage of this technique is the requirement for greater amount of fuel for an equivalent heat load.

A final combustion modification for reducing NO_x emissions is flue gas recirculation (JA-056). A portion of the gases are recycled back into the combustion chamber in front of the flame. The flue gas can be recycled either by free or forced draft systems. The recycled flue gases have two effects:

1) the temperature of the flame zone is reduced by the cool gases, and

2) the concentration of oxygen available for NO_x formation is reduced (JA-056).

A water or steam injection technique has been described for large gas-fired burners for the control of NO_x (JA-056). The injection of water or steam is probably unfeasible for process heaters due to problems involved with increased corrosion and decreased efficiency.

5.1.3.2 Fuel Modifications

The formation of NO_x can result from either the fixation of atmospheric N_2 or the conversion of fuel-bound nitrogen or both. Removal of nitrogen from air before combustion is impractical. Nitrogen which is held in liquid fuels, however, can be removed to various degrees by hydrogenation, which is usually done concurrently with hydrodesulfurization.

Additives such as metal oxides have some possibility to catalytically reduce or decompose NO to N_2. The emission reduction from this strategy is quite limited and the cost effectiveness is likely to be poor (BR-199).

An obvious solution to the reduction of NO_x emission would be to fire fuels containing smaller amounts of nitrogen. Natural gas contains less nitrogen per equivalent of energy than heavy fuel oil. The use of natural gas will, however, be determined by its availability. Low BTU gases such as the coke-gas are also expected to lower NO_x emissions due to reduced flame temperatures characteristics of the lower heating value fuels (BR-199).

5.1.3.3 Design Modifications

Design modifications of burners are also used to reduce NO_x emissions. Narrower spray angles which produce a low degree of atomization of the fuel have been found to give lower NO_x emissions (BA-003). Turbulence has also been found to affect NO_x production through entrainment of cooler gases. A burner which produces a long "lazy" flame has been found to produce less NO_x than an intense, short flame (BA-003).

Proper burner location and spacing also helps to reduce NO_x emissions. Burner arrangements which lower the flame temperature and radiate heat more easily are the most advantageous. Modifications such as tangential firing of burners do not allow flames to interact and thus lower the flame temperature. Tangential firing also enhances the radiation of heat as compared with front or opposite fired furnaces (BA-003).

5.1.3.4 Flue Gas Treating

Flue gas treating is still very much in the development stage. Combustion flue gas treating can be evaluated in the following general categories:

1) Catalytic decomposition,

2) Catalytic reduction,

   (a) Non-selective

   (b) Selective

3) Adsorption/reaction by solids, and

4) Absorption/reaction by liquids.

Denitrification of flue gas of oil-fired boilers or heaters is different from those burning fuel gas because:

- Catalysts which are used must be resistant to greater sulfur oxide and heavy metals concentrations for oil-fired heaters (OK-012),

- The particulates in flue gases from oil-fired units must be removed before entering and clogging the catalyst beds (OK-012), and

- Nitrogen oxide concentrations are generally higher for oil-fired heaters as compared to fuel gas-fired heaters (NA-005).

The four categories of flue gas treating processes mentioned above will be briefly described in the following sections.

Catalytic Decomposition

The decomposition of nitric oxide is thermodynamically favored. However, catalysts have been ineffective in enhancing the reaction rate. Little research has been conducted with concentrations of NO as low as those found in the flue gases (BA-003).

Catalytic Reduction

Nonselective reduction of NO_x occurs when the reducing agent such as H_2 or CH_4 reacts with other easily reduced compounds before reacting with the NO_x. A noble metal catalyst has been used to enhance the reaction rate of reduction. Noble metal catalysts would not be adaptable to flue gases because of sulfur poisoning. Experiments by Ryason and Harkins, however, show the reduction of both NO and SO_2 will occur in the presence of a copper on aluminum catalyst (BA-003). The major problem with this method is that the excess air must be finely controlled to allow little or no free O_2 in the flue gas. Environics presently have a noble metal catalytic reduction process on a gas-fired boiler in Los Angeles.

Selective reduction is much preferred to nonselective reduction in that it will allow the normal excess air used in firing a heater or boiler. In such a process, the reducing agent would be added to the flue gas in controlled amounts to selectively react with the NO to form N_2 and H_2O over a catalyst. Hydrogen, ammonia, carbon monoxide, and hydrogen sulfide have been selected as possible selective reductants. A possible flow scheme for H_2 or NH_3 selective reduction is shown in Figure 5.1-13. Ammonia reduction and H_2S or H_2 reduction have the added option of being also an SO_x removal system. The 90% removal of NO_x by ammonia reduction from an exhaust gas from a methanol process reformer with an NO_x concentration 200 ppm has been successfully accomplished on a commercial level by Japan's Sumitomo Chemical Company and Japan Gasoline Company (OK-012). The removal of NO by reaction with hydrogen sulfide and H_2 is presently in the experimental stages.

Adsorption/Reaction by Solids

A number of solid materials have been cited as adsorbents for NO_x. These materials include such common adsorbents as silica gel, alumina, char, and molecular sieves where adsorption is due primarily to physical forces, and metal oxides,

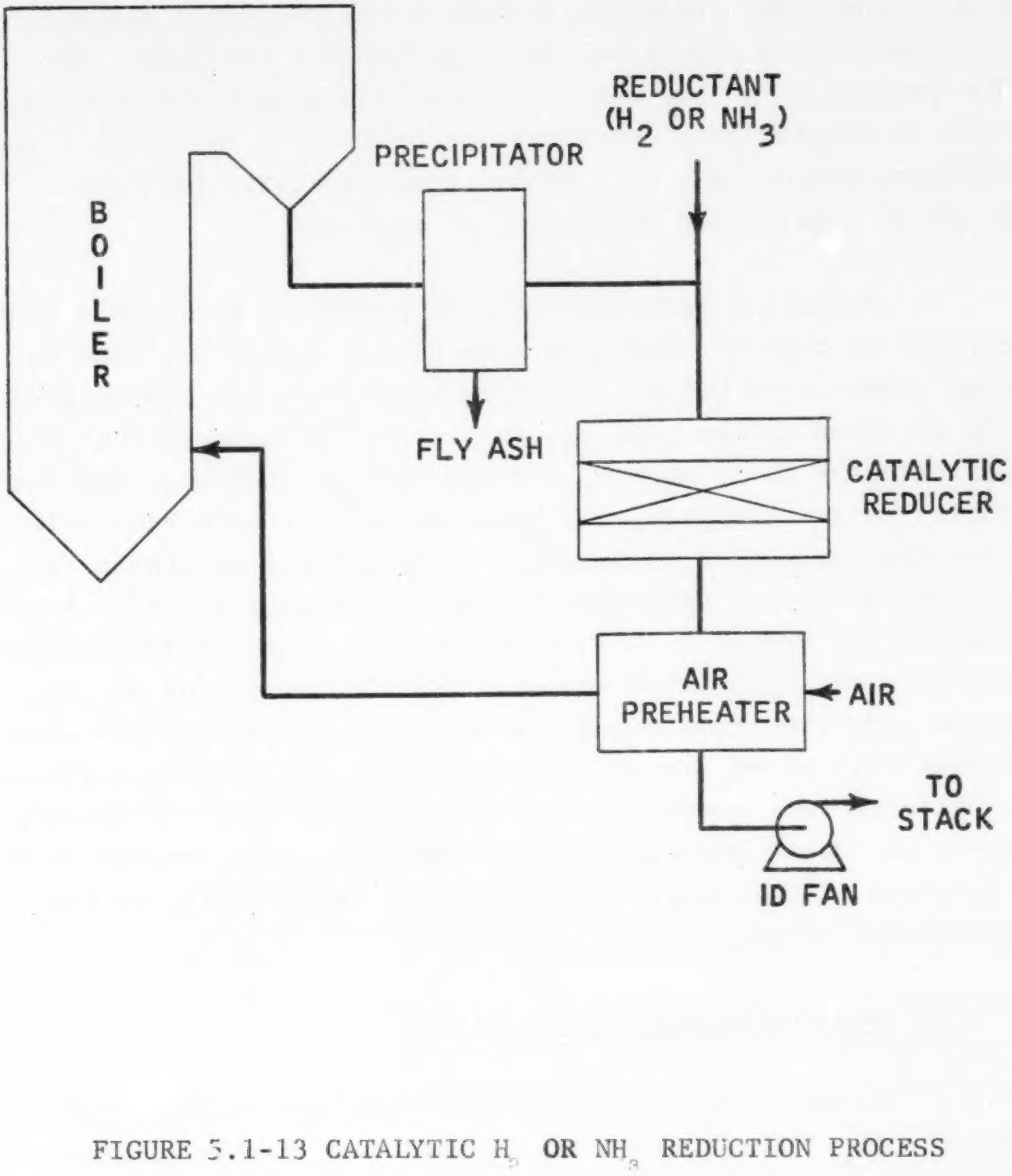

REDUCTANT
(H_2 OR NH_3)
PRECIPITATOR
BOILER
FLY ASH
CATALYTIC REDUCER
AIR PREHEATER
AIR
TO STACK
ID FAN

FIGURE 5.1-13 CATALYTIC H_2 OR NH_3 REDUCTION PROCESS

Source: (BA-003)

ion exchange resins, and hydroxides where attraction is principally chemical in nature (BA-003). An adsorbent containing 5 percent $NaC\ell O_2$ and 10 to 15 percent Na_2CO_3 supported on activated alumina can remove 100 percent of NO_x in gas streams containing low concentrations of NO_x. However, NO_x emission control by this method has been described as impractical since make-up costs for the oxidant are high (BA-003). Of the metal oxides, manganese and alkalized ferric oxides show the greatest technical potential. Problems that occur with solid systems are agglomeration of the fluidized bed due to molten nitrate salts in the regeneration process, attrition losses which require flue gas clean-up, and catalyst losses (BA-003).

Absorption/Reaction by Liquids

Aqueous absorption system appears to offer potential for combined NO_x and SO_x emission control but few results of development work have been published. Sulfuric acid scrubbing of NO_x has been investigated for large utility boilers by Tyco Laboratories (BA-003). The sulfuric acid process, as described by Tyco, is shown in Figure 5.1-14. One significant disadvantage of the sulfuric acid scrubber is that in order to remove a large percentage of NO from the original flue gas, the process must run at very high efficiency. The efficiency, however, is decreased by an increase in SO_2 concentration in the flue gas and by the presence of NO in the NO_2 recycle stream. Chiyoda Chemical Engineering Company has further developed the sulfuric acid scrubber to include a second absorption step where the NO_2 from an oxidation step which also oxidizes SO_2 to sulfuric acid is absorbed in an alkaline solution. Removal efficiencies for NO_x are claimed to range up to 95% (OG-010).

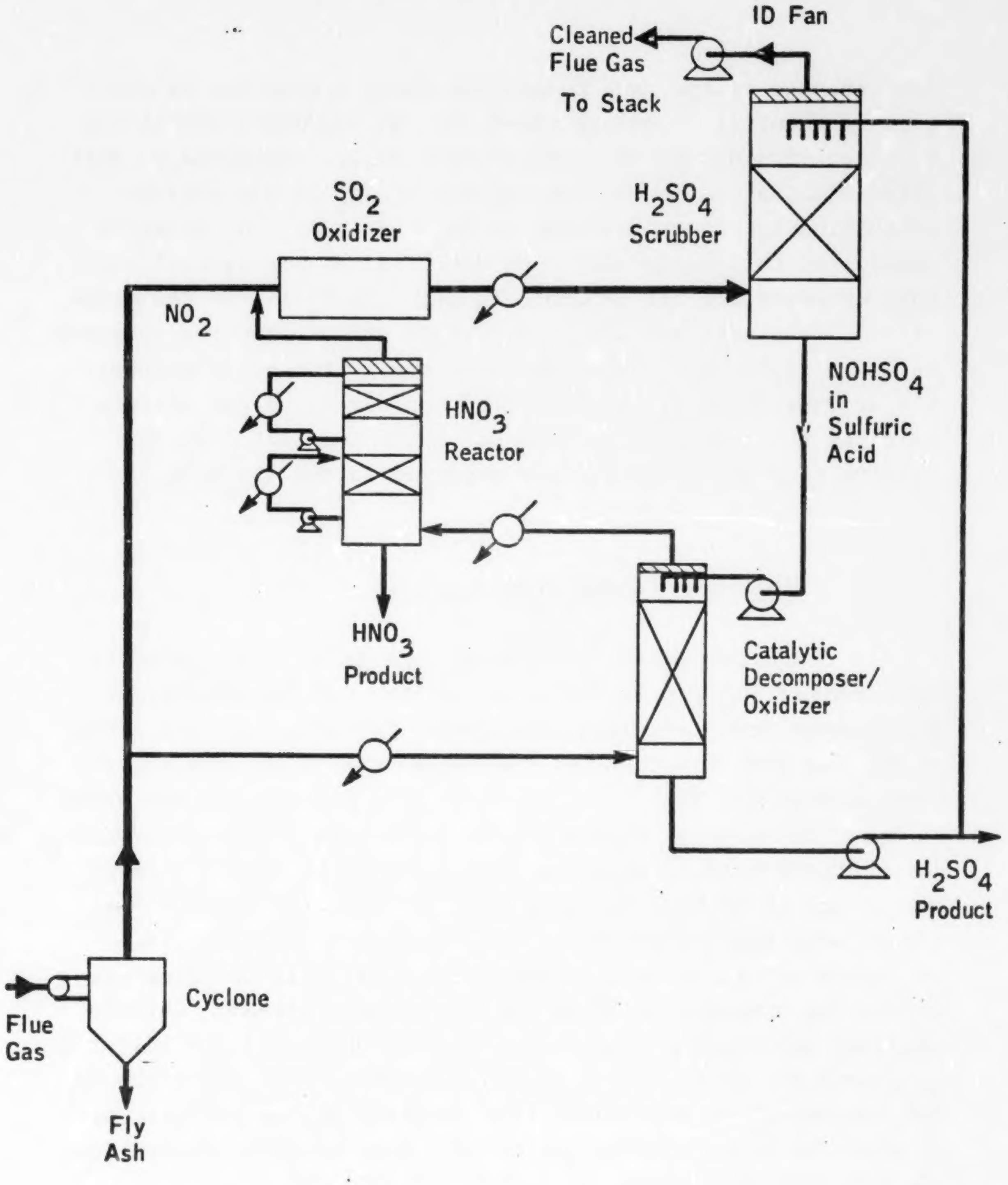

ID Fan
Cleaned Flue Gas
To Stack
SO_2 Oxidizer
H_2SO_4 Scrubber
NO_2
HNO_3 Reactor
$NOHSO_4$ in Sulfuric Acid
HNO_3 Product
Catalytic Decomposer/ Oxidizer
H_2SO_4 Product
Cyclone
Flue Gas
Fly Ash

FIGURE 5.1-14 TYCO'S ISOTHERMAL SULFURIC ACID SCRUBBING SYSTEM

Source: (BA-003)

5.1.3.5 NO_x Emissions From Incinerators

NO_x emissions from incinerators can be reduced by not incinerating at all. Landfill is the best alternative and has been described in the section on particulates removal. If the material is to be incinerated, a low firebox temperature and a low percentage of excess air are required to reduce NO_x. Some incinerators are fired with methane or fuel oil along with the incinerable sludge. This combination of combustion materials causes a substantial increase in the NO_x emission and should be avoided. NO_x emissions may also be decreased by recovering heat from the fire box by methods such as generating steam. By controlling the heat removed, the NO_x emissions can be controlled. Incinerators that reduce NO_x by changing combustion conditions are not available except on a developmental basis.

5.1.4 CO Emission Control

Atmospheric CO emissions from the refinery, LNG plant, and SNG plant come from process heaters, boilers, the CO boiler and the incinerator. CO emissions from process heaters and boilers can be controlled by (NA-004):

- Complete combustion
- Energy conservation
- Energy source substitution
- Gas cleaning
- Collection and flaring of miscellaneous CO emissions

Use of all of these methods will reduce CO emissions greatly in a refinery, LNG plant, or SNG plant.

Complete combustion is the best method for controlling CO emissions. Good practice includes proper design, application, installation, operation, and maintenance of process heaters and burners and auxiliary systems. Guides for good practices have been published by the fuel industry, equipment manufacturers, engineering associations, and government agencies (NA-004).

Probably the greatest factor in CO formation is the amount of excess air used in combusting fuels. A low excess air rate will result in incomplete oxidation of the carbon and the formation of CO. One must, however, be aware that a high excess air rate can have an effect of increasing CO production, also. With high excess air rates, the air cools the flame temperature which results in incomplete combustion.

Carbon monoxide emissions can be minimized by designing for (1) a high combustion temperature, (2) intimate contact among fuel, oxygen, and combustion gases, (3) sufficient reaction time, and (4) low effluent temperature (NA-004). Firing in excess of the design conditions is perhaps the greatest cause of excessive CO emissions from stationary sources. Proper choice of burners and good housekeeping practices as to cleaning burners will result in low CO emissions and better control of process heaters. Various types of burners and possible defects which will produce CO are shown in Table 5.1-5. Proper design of flue gas vent area is also highly desirable in that it allows for smooth flow of gases through the furnace with no back pressure to impede the air flow.

Energy conservation is an obvious method for reducing CO emissions, along with every other emission involved with combustion. Techniques such as preheating the furnace air and preheating the process side material result in lower loads on the heaters or furnaces and thusly, lower fuels combustion. Combustion control systems are also considered a source of energy conservation in that the most complete combustion will result in the greatest amount of energy released per unit mass of fuel.

Energy source substitution is also used to reduce CO emissions. The burning of natural gas will give about 35 times less CO per an equivalent of energy released as compared to fuel oil (NA-004). The availability of natural gas will, however, determine if it can be substituted for fuel oil. Also, if available, hydroelectric energy or nuclear energy as substitute for fossil fuels will reduce the total amount of CO emitted to the atmosphere.

TABLE 5.1-5

CLASSIFICATION OF OIL BURNERS ACCORDING TO APPLICATION AND LIST OF POSSIBLE DEFECTS

Burner type	Applications	Oil type usually used	Defects that cause excessive CO emissions
Commercial, Industrial Pressure atomizing	Steam boilers, process furnaces	No. 4, 5	Oil preheat too low or too high, nozzle wear, nozzle partly clogged, impaired air supply, clogged flue gas passages, poor draft, overloading
Horizontal rotary cup	Steam boilers, process furnaces	No. 4,5,6	Oil preheat too low or too high, burner partly clogged or dirty, impaired air supply, clogged flue gas passages, poor draft, overloading
Steam atomizing	Steam boilers, process furnaces	No. 5, 6	Oil preheat too low or too high, burner partly clogged or dirty, impaired air supply, clogged flue gas passages, poor draft, overloading, insufficient atomizing pressure
Air atomizing	Steam boilers, process furnaces	No. 5	Oil preheat too low or too high, burner partly clogged or dirty, impaired air supply, clogged flue gas passages, poor draft, overloading, insufficient atomizing pressure

SOURCE: (NA-004)

Gas cleaning is also a method for reducing CO emissions. For the refinery, LNG plant, and SNG plant, the only gas cleaning units are the shift converters on the hydrogen plant in the gasoline refinery and the SNG plant, and the CO boiler in the fluidized catalytic cracking unit.

The hydrogen plant is a steam-naphtha reforming process. The hydrogen synthesis reaction in the reforming process is the following (VO-025):

$$C_nH_m + nH_2O \rightarrow nCO + \frac{(2n+m)}{2} H_2$$

The CO produced is eliminated from the synthesis gas by a multiple shift conversion followed by a methanation of the residual carbon monoxide. The reactions for the carbon monoxide shift (1) and the methanation (2) are the following:

(1) $CO + H_2O \rightarrow CO_2 + H_2$

(2) $CO + 3H_2 \rightarrow CH_4 + H_2O$

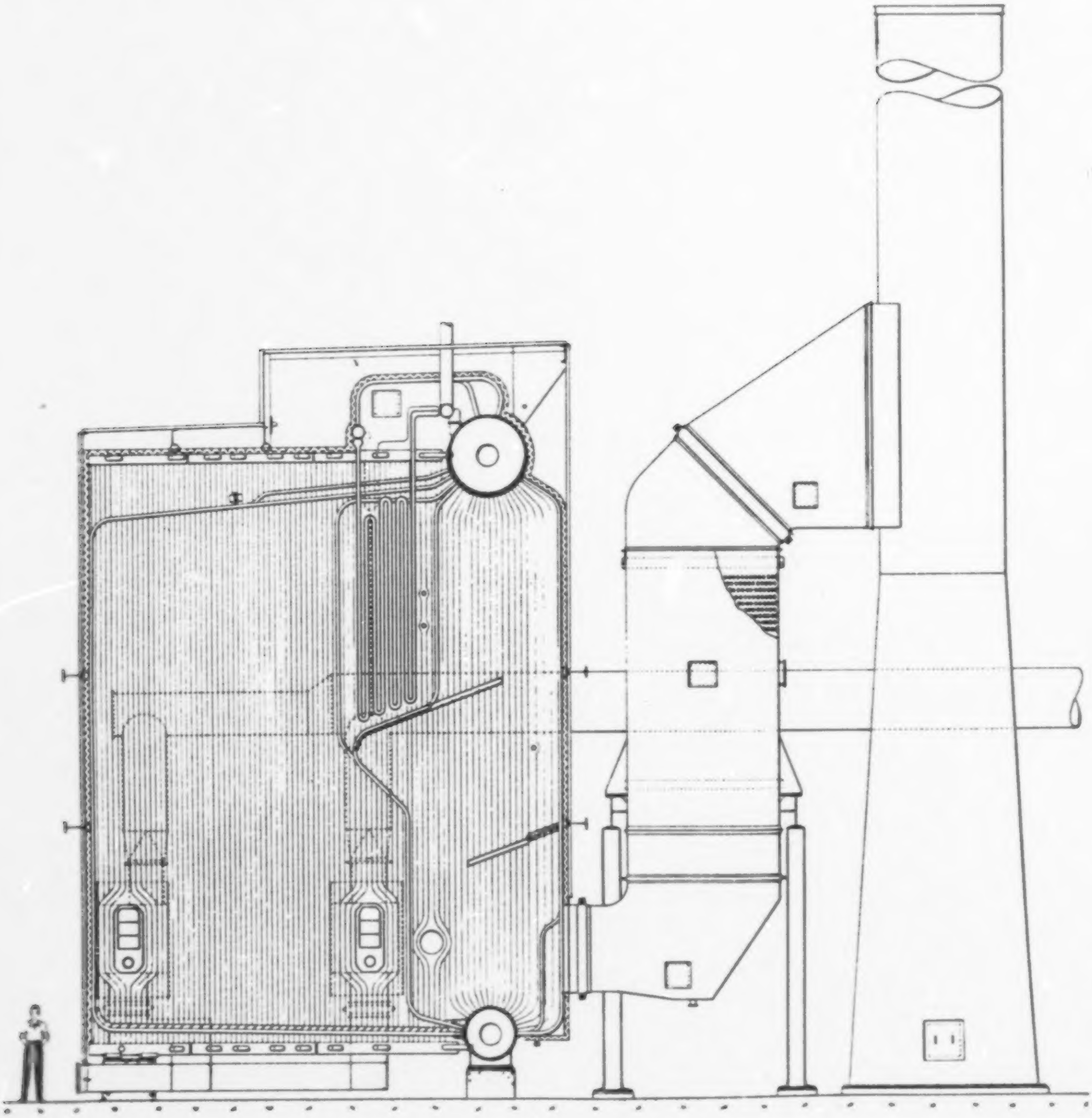
The final carbon dioxide produced is removed by absorption with MEA. Other CO_2 removal processes available include Giammarco-Vetrocoke, Benfield, Catacarb and Sulfinol.

The CO in the off-gas from the FCCU regenerator is removed in a CO boiler. The CO is burned to recover its heating value. In most cases supplementary fuel such as fuel oil is burned in the boiler to keep the combustion temperature at approximately 1800°F and to supply sufficient energy to produce steam. The average emission of CO from a FCCU regenerator is 13,700 pounds of CO per 1,000 barrels of fresh feed (NA-004). The CO boiler will reduce the carbon monoxide down to 100 to 150 ppm in the final effluent regenerator gas. A typical carbon monoxide waste-heat boiler is shown in Figure 5.1-15.

FIGURE 5.1-5

WATER-COOLED, CARBON MONOXIDE WASTE-HEAT BOILER

SOURCE: (DA-069).



5.1.5 Hydrocarbon Emissions Control

Hydrocarbon emission sources in the refinery, the LNG plant, and the SNG plant are many and quite varied. Some of the major refinery sources are storage tanks, fluidized catalytic cracking units, boilers and process heaters, the blowdown system, process drains, vacuum jets, and cooling towers. Hydrocarbon emissions from the LNG module are quite small and mainly due to gas-fired process heaters and boilers. Any storage of LNG on-site is in pressurized vessels which emit negligible amounts of hydrocarbons. The SNG module has hydrocarbon emissions from boilers and process heaters, storage, and the regenerator for the hot carbonate solution used for CO_2 absorption. As compared to the storage and regeneration process, the boiler and heaters give off negligible hydrocarbons. The following sections describe methods for controlling hydrocarbon emissions from these sources.

5.1.5.1 Carbonate Vent Gas

The hot carbonate system used in the SNG module (Benfield process) is used to reduce the CO_2 content in the final methane-fuel gas in order to increase the heating value of the gas. The regeneration of the potassium carbonate absorbent produces a large volume of CO_2 gas which has a typical hydrocarbon content of 0.027 wt percent (LO-095). Although the concentrations are very small, the total weight of hydrocarbon emitted is large because of the large volume of CO_2 vented to the atmosphere. The other CO_2 removal processes for upgrading synthesis gas use basically the same principle of high pressure (approximately 1,000 psig) absorption of the CO_2 (and H_2S) and removal from the absorbent by a depressurized regeneration process and thus are expected to emit equivalent amounts of hydrocarbons.

A possible control method for hydrocarbon emissions is to route the off-gas to a boiler or process heater to combust the hydrocarbons. One would gain the heat of combustion of the hydrocarbons, but would lose the energy which is required in sensible heating of the inert off-gas (mainly CO_2). Another possible control method is by first partially flashing off-gas from the rich absorbent solution and recycling this gas back through the absorber. The flashed gas is expected to contain an appreciably higher concentration of hydrocarbons than the directly vented regenerator gas, because hydrocarbons have a much lower solubility in the absorbent solution than the CO_2 or H_2S.

5.1.5.2 Storage Control

A major hydrocarbon emission source in the petroleum industry is tankage. Storage emissions depend on diurnal temperature and pressure changes, filling operations, volatilization, solar radiation, and mechanical condition of the tanks.

Proper design of storage tanks will control hydrocarbon emissions greatly. There are five basic types of storage tanks used in the petroleum industry. These are: fixed roof, floating roof, internal floating cover, variable space, and pressure. The applicability of these tanks largely depends on the volatility of the stored liquid. Table 5.1-6 shows the type of tank generally used for storing certain volatile petroleum products (EN-043, MS-001).

TABLE 5.1-6

NATURE OF PRODUCT STORAGE AT REFINERIES

Product	True Vapor Pressure psia @ 60°F	Types of Storage Tanks	Qty. Stored 1968 (10^6 bbl)
Fuel Gas	---	Cryogenic - Pressurized	
Propane	105	Pressurized	
Butane	26	Pressurized	
Motor Gasoline	4-6	Variable Space, Fixed Roof, Floating Roof	204
Aviation Gasoline	2.5-3	Variable Space, Fixed Roof, Floating Roof	14
Jet Naphtha	1.1	Variable Space, Fixed Roof, Floating Roof	18
Jet Kerosene	<0.1	Fixed Roof	31
Kerosene	<0.1	Fixed Roof	46
No. 2 Distillate	<0.1	Fixed Roof	346
No. 6 Residual	<0.1	Fixed Roof	
Crude Oil	2	Variable Space, Fixed Roof, Floating Roof	137

From a hydrocarbon emissions standpoint, any storage facility which is flexible enough to retain all vapors emitted from the stored hydrocarbon at an economically feasible level is the system most desirable. The fixed roof tank is the only tank mentioned above which is not designed for containing vapors emitted. Usually, in a fixed roof tank, the vapors are vented to the atmosphere through a pressure-vacuum vent. The variable space-type storage tank is designed to control normal diurnal breathing losses and small filling operations. Large changes in the vapor content can not be handled by the variable space tank alone and thus vapors will have to be vented to the atmosphere. Pressure vessels are used to hold highly volatile petroleum products under pressure. The shape of the pressure vessel depends on the pressure required. Spheres can be operated at pressures up to 217 psi; spheroids, up to 50 psi; noded spheroids, up to 20 psi; and plain or noded hemispheroids, up to 75 psi and 2½ psi, respectively (DA-069).

Floating Roof Tanks

The floating roof tank is the most commonly used tank for controlling hydrocarbon emissions. Modern designs include pontoon deck floating roofs, double-deck floating roofs, and trussed-pan floating roofs. The major concerns in design of the roof are structural support and reduction of heat conduction due to solar radiation. The floating roof is constructed about eight inches shorter in diameter than the inside tank diameter.

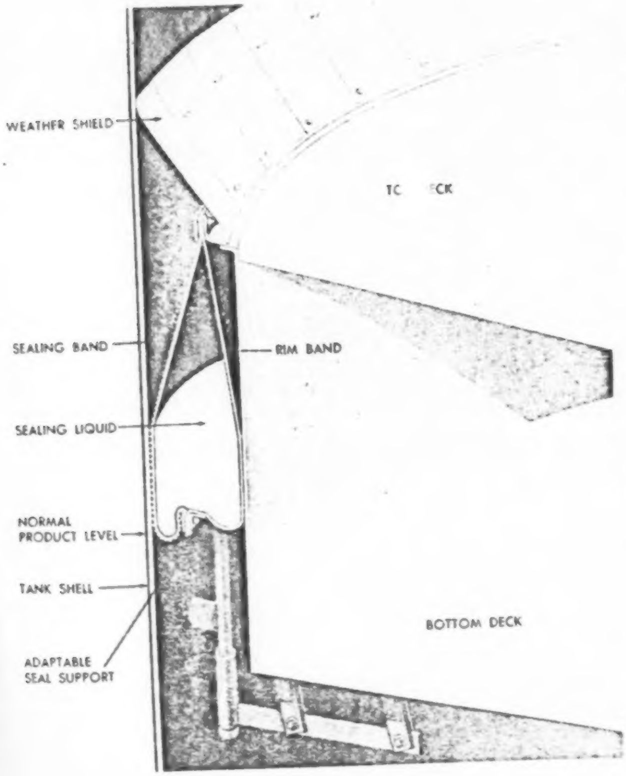
The space between is usually sealed by vertical shoes (metal plates) connected by braces to the floating roof. A fabric seal is also included to reduce hydrocarbon emissions. The space between the roof and the wall is the greatest source of emissions from a floating roof tank. Frequently an additional secondary seal is added to act as a wiper reducing the wicking action associated with floating roof tanks (NA-032). Another sealing device is a flexible tube which floats on the liquid surface and keeps contact between the roof and the tank wall. Different tube seals are shown in Figure 5.1-16. Floating roof tanks are about 91 percent efficient in controlling hydrocarbon emissions from gasoline storage (EN-071).

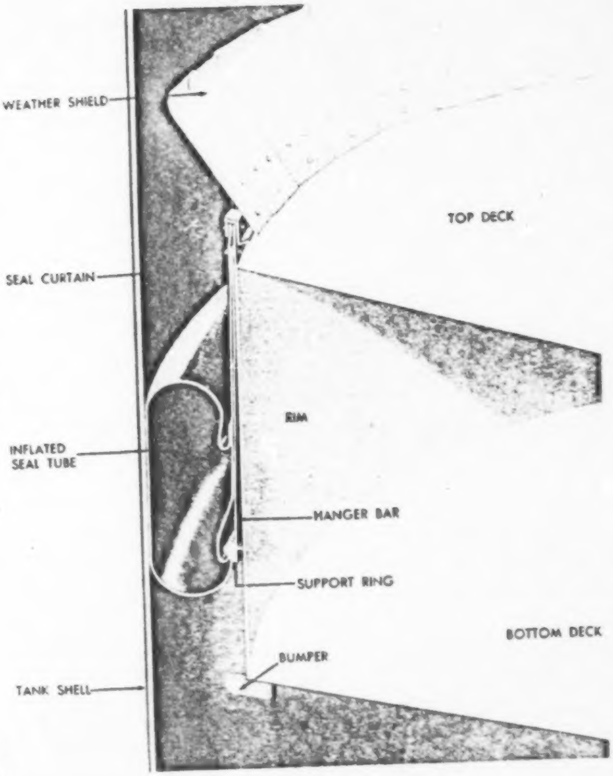
Fixed Roof Tanks

In order to limit emissions from fixed roof tanks, floating covers have been designed. One type is a floating plastic blanket. The blanket is constructed with plastic floats underneath and custom manufactured so that only a one-inch gap remains around the periphery (DA-069). A skirt is placed above this gap to further eliminate fugitive vapors. Another new technique in sealing fixed roof tanks is a floating microsphere blanket. The microspheres are made of plastic resins less dense than the liquid petroleum product. The microspheres entirely cover the liquid surface and their fluidity gives the added advantage of being able to flow around internal tank parts.

Vapor Recovery System

With present day prices of petroleum products increasing, more sophisticated systems for recovering hydrocarbon vapors are becoming economically feasible. One system employed is an integrated vapor recovery system. The vapor recovery system is a closed system which is set up to recover hydrocarbon vapors


WEATHER SHIELD
TOP DECK
SEALING BAND
RIM BAND
SEALING LIQUID
NORMAL PRODUCT LEVEL
TANK SHELL
BOTTOM DECK
ADAPTABLE SEAL SUPPORT


WEATHER SHIELD
TOP DECK
SEAL CURTAIN
RIM
INFLATED SEAL TUBE
HANGER BAR
SUPPORT RING
BOTTOM DECK
BUMPER
TANK SHELL

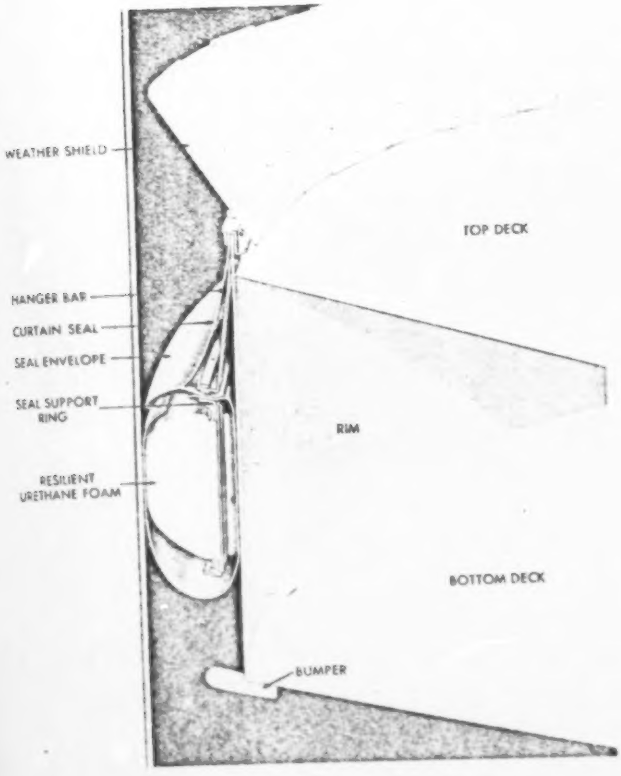

WEATHER SHIELD
TOP DECK
HANGER BAR
CURTAIN SEAL
SEAL ENVELOPE
SEAL SUPPORT RING
RIM
RESILIENT URETHANE FOAM
BOTTOM DECK
BUMPER

FIGURE 5.1-16.

SEALING DEVICES FOR FLOATING-ROOF TANKS:

Liquid-Filled Tube Seal (Upper Left)

Inflated Tube Seal (Upper Right)

Foam-Filled Tube Seal (Chicago Bridge and Iron Co., Chicago, Illinois) (Lower Left)

Source: (DA-069)

emitted from storage facilities and also the loading facilities. A typical vapor recovery system including a vapor saver is shown in Figure 5.1-17. The variable space tank included is designed to control breathing losses and small vapor changes within the system. The vapor recovery unit which handles large vapor volume changes such as during loading operations or periods of drastic ambient temperature or pressure changes includes a compressor-refrigeration system. Vapor recovery units can liquefy hydrocarbon vapors by several principles which include compression-refrigeration, absorption, and adsorption. They also can employ a combination of these principles. The efficiency of vapor recovery units typically ranges from 90% to 95%, depending upon the composition and concentration of the hydrocarbon vapors processed (EN-071). Vapor recovery units are manifolded into the vapor collection systems of tankage and loading operations for the reliquefaction of hydrocarbon vapors into product. Vapor recovery systems are quite expensive as compared to floating roof tanks, and only give a little greater efficiency in recovering vapors.

Another possible control technique is maintaining wet scrubbers or condensers on the vents of fixed roof tanks. The wet scrubbers can be bubble-cap tray towers, packed towers, spray towers, or Venturi scrubbers. These types of scrubbers are shown in Figure 5.1-18. The common absorbents for organic vapors are water, mineral oil, nonvolatile hydrocarbon oils, and aqueous solutions (e.g., solutions of oxidizing agents, sodium carbonate, or sodium hydroxide). If water is used, the hydrocarbon rich water is sent to a closed waste water stream to be treated at the waste water treatment facility. The other absorbents can be regenerated, with the collected hydrocarbons flared or recycled, depending on the amounts recovered.

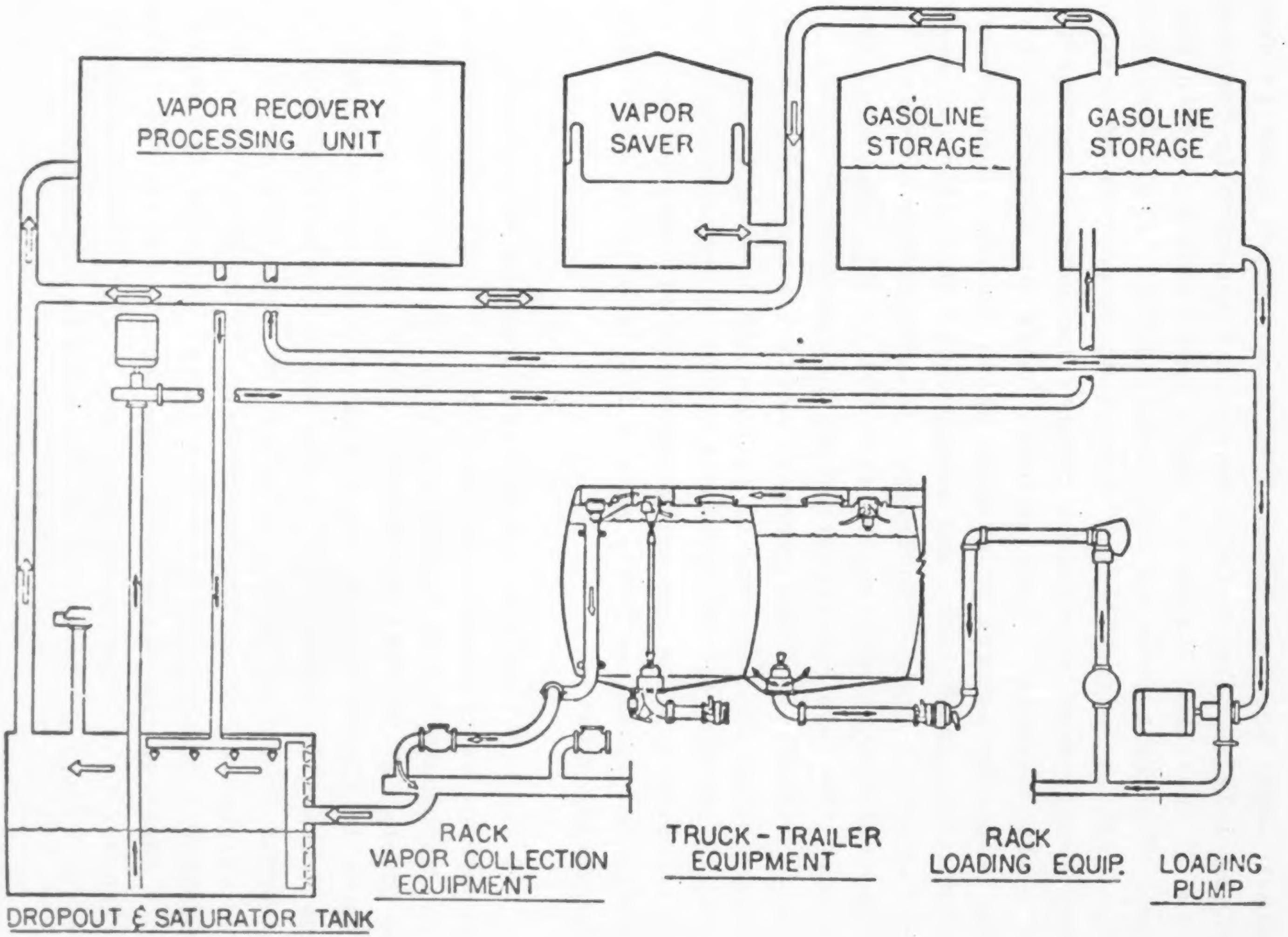
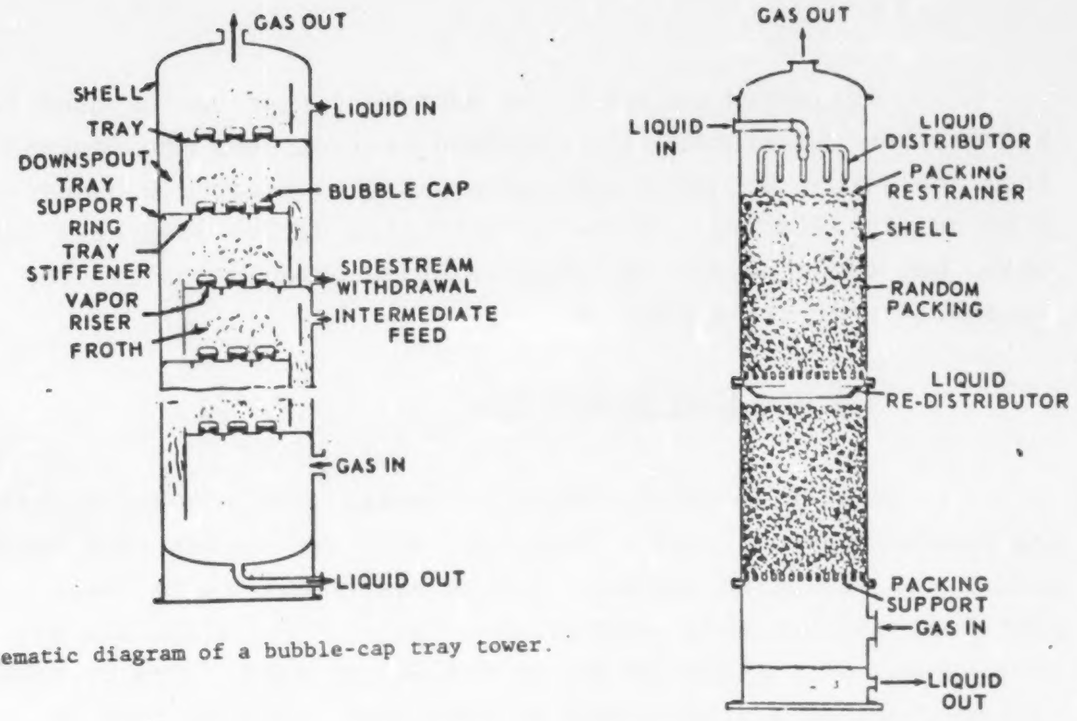
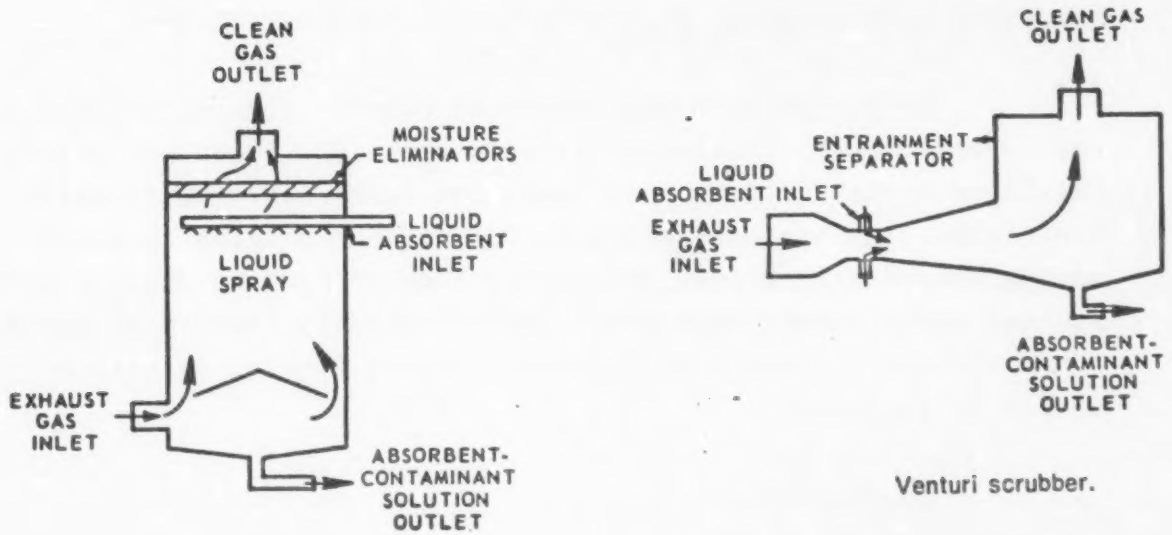

VAPOR RECOVERY PROCESSING UNIT
VAPOR SAVER
GASOLINE STORAGE
GASOLINE STORAGE
DROPOUT & SATURATOR TANK
RACK VAPOR COLLECTION EQUIPMENT
TRUCK - TRAILER EQUIPMENT
RACK LOADING EQUIP.
LOADING PUMP

FIGURE 5.1-17 COMPLETE VAPOR RECOVERY SYSTEM


GAS OUT
SHELL
TRAY
DOWNSPOUT
TRAY SUPPORT RING
TRAY STIFFENER
VAPOR RISER
FROTH
LIQUID IN
BUBBLE CAP
SIDESTREAM WITHDRAWAL
INTERMEDIATE FEED
GAS IN
LIQUID OUT
GAS OUT
LIQUID IN
LIQUID DISTRIBUTOR
PACKING RESTRAINER
SHELL
RANDOM PACKING
LIQUID RE-DISTRIBUTOR
PACKING SUPPORT
GAS IN
LIQUID OUT

Schematic diagram of a bubble-cap tray tower.

Packed tower.


CLEAN GAS OUTLET
MOISTURE ELIMINATORS
LIQUID ABSORBENT INLET
LIQUID SPRAY
EXHAUST GAS INLET
ABSORBENT-CONTAMINANT SOLUTION OUTLET
CLEAN GAS OUTLET
ENTRAINMENT SEPARATOR
LIQUID ABSORBENT INLET
EXHAUST GAS INLET
ABSORBENT-CONTAMINANT SOLUTION OUTLET

Venturi scrubber.

Spray tower.

FIGURE 5.1-18 HYDROCARBON VAPOR SCRUBBERS
SOURCE: (NA-032)

Activated carbon is an adsorbent that can be used for hydrocarbon emissions. The adsorbed hydrocarbons are removed from the carbon by steam stripping and then recovered by decantation or distillation. Costs of activated carbon adsorbers are high, but the recovery of valuable hydrocarbons enhances the feasibility of the operation.

Storage Tank Maintenance

Heat from solar radiation causes problems by increasing hydrocarbon boil-off. Painting tanks and proper tank design reduce the radiation effect. Paints are chosen as to those that best reflect solar radiation. Table 5.1-7 lists the effectiveness of various paints on reflecting heat. Proper tank design includes a double-deck pontoon-type floating roof or trussed floating roof to avoid direct warm metal-liquid contact. Tank diameter also effects the amount of hydrocarbon emitted. A smaller tank diameter will have less emissions (DA-069).

Proper maintenance practices help to eliminate hydrocarbon emissions. Particular trouble spots are leaky and poorly regulated vents on fixed roof tanks and leaky seals on floating roof tanks. Maintaining properly painted tanks helps in eliminating emissions. Proper scheduling such as pumping liquids into storage tanks during cool hours and withdrawing liquids at hotter times and maintaining short periods between pumping operations should be followed.

1.5.3 Loading Rack Controls

Hydrocarbon emissions from transport loading operations are generally controlled by the use of a vapor collection device manifolded into a vapor recovery unit (see Figure 5.1-17). The transport vehicle may be a tank truck, rail car, barge, or marine vessel.

TABLE 5.1-7

RELATIVE EFFECTIVENESS OF PAINTS IN KEEPING TANKS FROM WARMING IN THE SUN (Nelson, 1953)

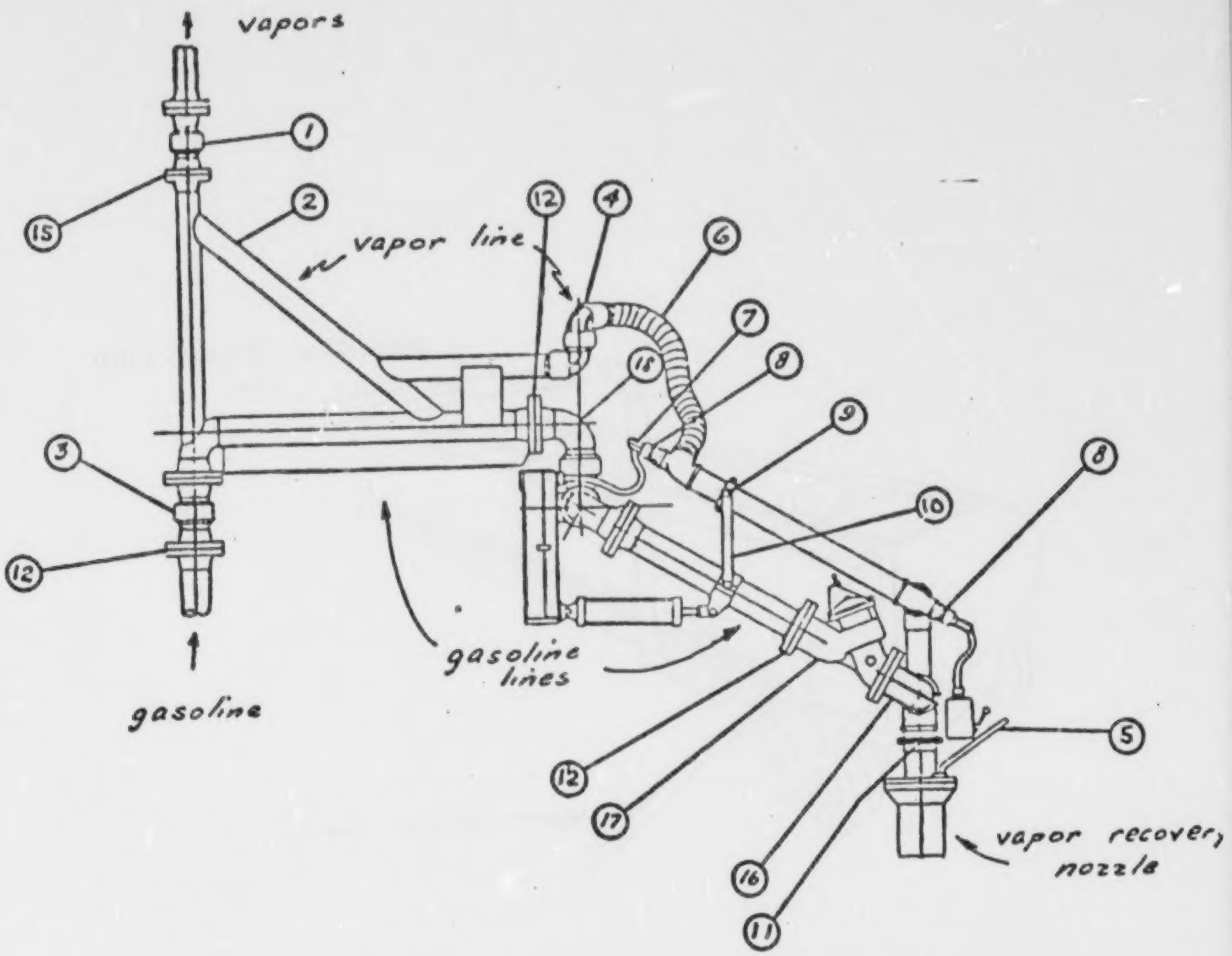
Color	Relative effectiveness as reflector or rejector of heat, %
Black	0
No paint	10.0
Red (bright)	17.2
Red (dark)	21.3
Green (dark)	21.3
Red	27.6
Aluminum (weathered)	35.5
Green (dark chrome)	40.4
Green	40.8
Blue	45.5
Gray	47.0
Blue (dark Prussian)	49.5
Yellow	56.5
Gray (light)	57.0
Aluminum	59.2
Tan	64.5
Aluminum (new)	67.0
Red iron oxide	69.5
Cream or pale blue	72.8
Green (light)	78.5
Gray (glossy)	81.0
Blue (light)	85.0
Pink (light)	86.5
Cream (light)	88.5
White	90.0
Tin plate	97.5
Mirror or sun shaded	100.0

The type of vapor collection system installed depends on how the transport vehicle is loaded. If the unit is top loaded, vapors are recovered through a top loading arm (Figure 5.1-19). Product is loaded through a central channel in the nozzle. Displaced vapors from the compartment being loaded flow into an annular vapor space surrounding the central channel and in turn flow into a hose leading to a vapor recovery system.

If the transport is bottom loaded, the equipment needed to recover the vapor is considerably less complicated. Vapor and liquid lines are independent of each other with resultant simplification of design. Figure 5.1-20 shows a typical installation. Product is dispensed into the bottom of the transport and displaced vapors are collected from the tank vents and returned to a vapor recovery unit.

Bottom loading vapor recovery has many advantages over top loading vapor recovery. Bottom loading generates much less vapor, generates almost no mist and is safer from a static electricity point of view.

The vapor collection efficiency of loading controls is in excess of 95 percent. However, the overall emission reduction is also dependent on the efficiency of the vapor recovery unit. A 90 percent efficient vapor recovery unit would make a loading control system 85 percent efficient.


vapors
1
15
2
vapor line
12
4
6
18
7
8
9
10
3
12
8
gasoline lines
gasoline
5
12
17
16
11
vapor recovery nozzle

MISCELLANEOUS PARTS

ITEM	PART NO.	DESCRIPTION	QTY.
1	3420-F-30	Swivel Joint, 3"	1
2	2775 •	Boom	1
3	3420-F-40	Swivel Joint, 4"	1
4	H-5936	Swivel Joint 3"	1
5	D-837-M	Handle	1
6	H-5898-RP	Hose	1
7	H-5906-M	Elbow	1
8	H-5905-M	Cord Grip	2
9	H-5818-	Collar Sub-Assembly	2
10	C-1667-A	Link	2
11	C-2479-M	Gasket	1

ITEM	PART NO.	DESCRIPTION	QTY.
12	H-4190-M	Gasket, 4"	6
13	D-836-M	Upper Handle & Pipe	1
14	3630-30	Swivel Joint, 3"	1
15	H-4189-M	Gasket, 3" :	1
16	H-5952	Swivel Joint Sub-Assembly, 4"	
	3840-FO-40	Swivel Joint Only	1
	710	4 x 2 7.8 Nipple Only	1
	C-555-A	4" Flange Only	1
17	417-FKA-4"	Loading Valve	1
18	3476-F-40	Swivel Joint, 4"	1

FIGURE 5.1-19 TOP LOADING ARM EQUIPPED WITH A VAPOR RECOVERY NOZZLE

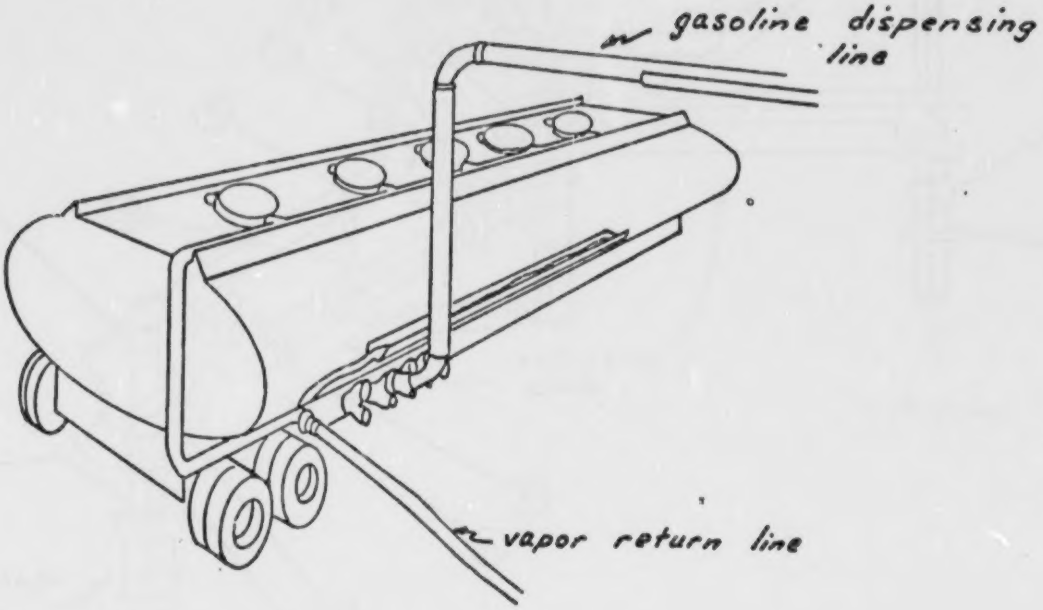

gasoline dispensing line
vapor return line

FIGURE 5.1-20 BOTTOM LOADING VAPOR RECOVERY SYSTEM

5.1.5.4 Combustion Source Controls

Hydrocarbon emissions from process heaters and steam boilers can be minimized by adjusting the fuel to air ratio for optimum fuel combustion. To insure optimum combustion conditions are maintained, some refineries have installed oxygen analyzers and smoke alarms on heater and boiler stacks (WA-086). For process heaters that do emit large quantities of hydrocarbons, catalytic afterburners can be used. The use of the afterburners, however, requires additional fuel for complete combustion of the hydrocarbons. The catalyst allows the combustion to take place at a lower temperature (NA-032). A catalytic afterburner is shown in Figure 5.1-21.

Internal combustion engines used to drive older compressors have inherently high hydrocarbon emissions. The major means of controlling hydrocarbon emissions from this source is by carburetion adjustments similar to those applied to automobile engines for emission control. Economic considerations coupled with increased concern for emission reductions is inducing refineries to phase out the use of internal combustion engines.

5.1.5.5 Incinerators

The best possible way to eliminate hydrocarbon emissions from sludge incineration is by disposing of the material by landfill. This operation is described in the section on Solids Emissions Control.

If the sludge is incinerated, auxiliary burners are used for secondary combustion of the wastes. The auxiliary burners will increase the incineration temperature in certain locations to promote the reduction of hydrocarbons. Good contact between the combustible material and air will also reduce hydrocarbon emission. Good contact is promoted by baffling of the physical mixing apparatus, introducing air at strategic locations, and locating auxiliary burners to promote mixing (NA-032).

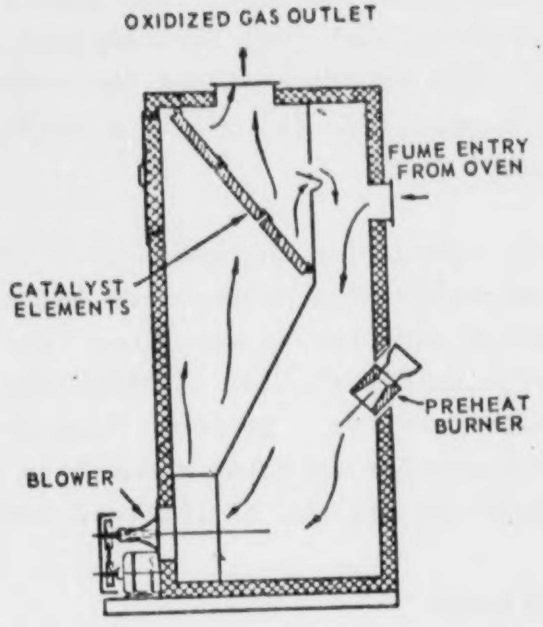

OXIDIZED GAS OUTLET
FUME ENTRY FROM OVEN
CATALYST ELEMENTS
PREHEAT BURNER
BLOWER

FIGURE 5.1-21 CATALYTIC AFTERBURNER

As an indirect method of reducing hydrocarbons, the heat from incineration can be recovered and used to produce steam. The heat load recovered would mean a reduction in fuel needed to produce steam within the refinery where the sludge incinerator is located.

5.1.5.6 Process Source Controls

Catalytic Cracker Regenerators

There are two major control measures applicable to the reduction of hydrocarbon emissions in the flue gas of catalytic cracker regenerators. The first of these is incineration in a carbon monoxide waste-heat boiler. By incinerating regenerator flue gas in CO waste-heat boilers, the hydrocarbon emissions are reduced to a neglibible amount and valuable thermal energy is recovered from the flue gas.

A second control measure applicable to the flue gas from moving bed catalytic cracker regenerators as well as the flue gas from regenerating operations for other catalysts is incineration in a heater fire box or smoke plume burner. These regenerators produce significantly less flue gas than FCC regenerators and may not justify a CO boiler. Catalysts in this category may include reformer, isomerization, and hydrocracking catalysts. Hydrocarbon emissions in regenerator flue gas are reduced to negligible quantities by incineration in heater fire-boxes and smoke plume burners.

Although neither CO boilers nor other forms of regenerator flue gas incineration are extensively used today, they are becoming standard equipment in new refineries and expansions of existing units. This is a result of both energy conservation and increased concern for air quality.

Vacuum Jets - Barometric Condensers

Hydrocarbon emissions from barometric condensers on vacuum jets are attributable to both the venting of non-condensable hydrocarbons as well as to the evaporation of hydrocarbons from the oily barometric condensates.

Three measures for minimizing oily condensate generation are mechanical vacuum pumps, lean oil absorption, and surface condensers. While mechanical vacuum pumps have little effect on the quantity of non-condensable hydrocarbons generated, they do eliminate the generation of oily steam condensate. The insertion of a lean oil absorption unit between the vacuum tower and the first stage vacuum jet helps to minimize the quantities of both non-condensables and oily condensate (AM-055). The rich oil effluent is reused as charge stock and not regenerated. Surface condensers in place of barometric condensers minimize oily condensates but have little effect on the quantity of non-condensables (AT-040).

Because there are no means to completely eliminate the generation of non-condensable vapors from vacuum pumps or steam ejectors, these emissions must be controlled by either vapor incinerators or vapor recovery units. Vapor incinerators combust the vapors by catalytic or direct flame methods. Vapor recovery units on the other hand recover the hydrocarbon vapors and return them to processing streams.

The maximum degree of control attainable for the hydrocarbon vapors from vacuum jets equipped with barometric condensers is effectively 100 percent (AT-040). Currently however, controls for vacuum units are not widely applied in the petroleum industry.

Blowdown Systems

Blowdown emissions can be effectively controlled by venting into an integrated vapor-liquid recovery system. All units and equipment subject to shutdowns, upsets, emergency venting, and purging are manifolded into a multi-pressure collection system. Discharges into the collection system are segregated according to their operating pressures. A series of flash drums and condensers arranged in descending pressures separates the blowdown into vapor pressure cuts. These recovered gaseous and liquid cuts can be either flared and/or re-refined. A typical flaring system is shown in Figure 5.1-22.

Fully integrated blowdown recovery systems can reduce refinery blowdown emissions to 5 lbs of hydrocarbon/10^3bbl of refinery feed (AT-040). Because most refineries are currently applying some degree of blowdown system control the average refinery emissions from blowdown systems range from 120 lbs to 200 lbs of hydrocarbons/10^3bbl of refinery feed (MS-001, AT-040).

Process Drains and Waste Water Separators

Control measures for reducing the evaporative hydrocarbon emissions from process drains and waste water separators center around 1) reducing the quantity of hydrocarbons evaporated, and 2) enclosing the waste water systems.

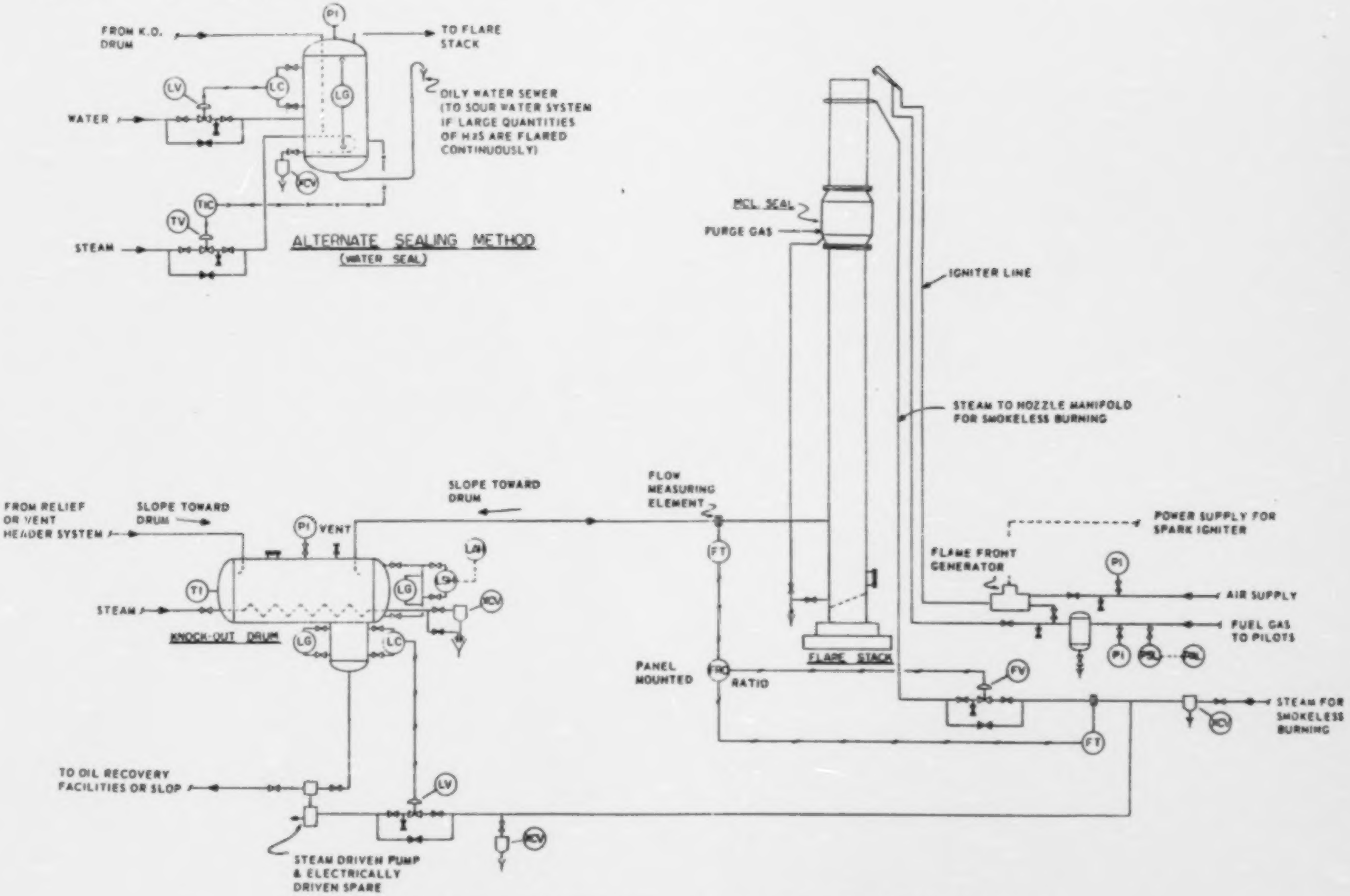
The quantity of hydrocarbons evaporated can first be reduced by minimizing through good housekeeping the volume of oil leaked to the waste water systems. Lowering the temperature of the waste water will also reduce hydrocarbon evaporation (AM-055).

Measures for enclosing waste water systems include manhole covers, catch basin liquid seals, and fixed or floating roofs for API separators. The potential also exists for some form of vapor disposal or vapor recovery device in conjunction with fixed roofs on API separators (EL-033).

FIGURE 5.1-22

TYPICAL FLARE INSTALLATION

SOURCE: (AM-055)


FROM K.O. DRUM
TO FLARE STACK
PI
LV
LC
LG
WATER
OILY WATER SEWER (TO SOUR WATER SYSTEM IF LARGE QUANTITIES OF H2S ARE FLARED CONTINUOUSLY)
PCV
TIC
TV
STEAM
ALTERNATE SEALING METHOD (WATER SEAL)
MCL SEAL
PURGE GAS
IGNITER LINE
STEAM TO NOZZLE MANIFOLD FOR SMOKELESS BURNING
FROM RELIEF OR VENT HEADER SYSTEM
SLOPE TOWARD DRUM
VENT
SLOPE TOWARD DRUM
FLOW MEASURING ELEMENT
LAH
LSH
PCV
TI
STEAM
KNOCK-OUT DRUM
LG
LC
FT
PANEL MOUNTED
FRC
RATIO
FLARE STACK
POWER SUPPLY FOR SPARK IGNITER
FLAME FRONT GENERATOR
AIR SUPPLY
FUEL GAS TO PILOTS
PSL
PAL
FV
FT
STEAM FOR SMOKELESS BURNING
TO OIL RECOVERY FACILITIES OR SLOP
LV
PCV
STEAM DRIVEN PUMP & ELECTRICALLY DRIVEN SPARE

Note: This represents an operable system arrangement and its components. Arrangement of the system will vary with the performance required. Correspondingly, the selection of types and quantities of components, as well as their applications, must match the needs of the particular plant and its specifications.

Studies of Los Angeles County refineries indicate that hydrocarbon emissions from controlled waste water systems are as low as 10 lbs/10^3 bbl of refinery feed (AT-040). On a nationwide basis and accounting for the existing degree of control, it is estimated that hydrocarbon emissions from waste water systems in 1972 averaged 105 lbs/10^3 bbl refinery feed (MS-001).

Cooling Towers

The control of hydrocarbon emissions from cooling towers is best effected at the point where hydrocarbon contaminants enter the cooling water. Hence, systems for detection of contamination in water, proper maintenance, speedy repair of leaks, and good housekeeping programs in general are necessary to minimize the air pollution occurring at the cooling tower. In addition, water that has been used in direct contact condensers should be eliminated from cooling towers. Greater use of air cooling will also control hydrocarbon emissions by reducing the size of the cooling water system (DA-069).

Refineries practicing good housekeeping in Los Angeles County have succeeded in reducing their cooling tower emissions to approximately 10 lbs/10^3 bbl refinery feed (AT-040, AM-055).

5.1.5.7 Fugitive Source Controls

Although inconspicuous, fugitive hydrocarbon emission sources are generally significant because of their abundance. Regular maintenance and good housekeeping are the major control measures for minimizing fugitive hydrocarbon emissions.

Pumps and Compressor Seals

Pump and compressor seals inherently leak and there are no practical means for eliminating hydrocarbon emissions from these sources. As brought out in the section on fugitive emissions, the emissions from centrifugal pumps with mechanical seals average 3.2 lbs/day-seal and from centrifugal pumps with packed seals average 4.8 lbs/day-seal. Therefore, a 33 percent reduction in hydrocarbon emissions from centrifugal pumps may be effected by installing mechanical seals in place of packed seals. There are no alternatives to using packed seals on reciprocating pumps. Dual sets of seals may also be installed with provisions to vent the volatile vapors that leak past the first seal into a vapor recovery system.

Frequent inspection and maintenance of seals are very important measures for the minimization of pump and compressor leaks.

Pressure Relief Valves

Hydrocarbon emissions from pressure relief valves are sometimes controlled by manifolding to a vapor control device or a blowdown system (DA-069). For valves where it is not desirable, because of convenience or safety aspects, to discharge into a closed system frangible blanks called rupture discs can be installed before the valve. Rupture discs serve to prevent the pressure relief valve from leaking as well as protect the valve seat from corrosive environments (WA-086).

The hydrocarbon emissions from relief valves controlled by rupture discs or blowdown systems are negligible.

Pipeline Valves and Flanges

Hydrocarbon emissions originating from product leaks at valves and flanges can be controlled by regular inspection and prompt maintenance of valve packing boxes and flange gaskets. Because of its dependence on the nature of the products handled, the degree of maintenance, and the characteristics of the equipment, the emissions reduction from controlling valves and flanges is undefinable.

Pipeline Blind Changing

Emissions from the changing of blinds can be minimized by pumping out the pipeline and then flushing the line with water before breaking the flange. Slight vacuums can be maintained in the pipeline for the case of highly volatile hydrocarbons. Spillage can also be minimized by the use of special "line" blinds in place of the common "slip" blinds. A survey of Los Angeles County refineries indicated that spillage from line blinds was 40 percent of the spillage for slip blinds. In addition, combinations of line blinds in conjunction with gate valves allow changing of line blinds while the pipeline is under pressure (DA-069).

Purging Sampling Lines

One means for controlling the hydrocarbon emissions generated by purging sampling lines is the installation of drains and flushing facilities at each sample point. Conscious efforts to avoid excessive sampling in addition to flushing sample purges into the drain have a significant impact on the hydrocarbon emissions from sampling operations.

Miscellaneous Emissions

There are several other fugitive emission sources which are collectively significant but not common to all refineries and not easily identifiable. The control of these sources is basically centered around regular inspection, proper maintenance, and good housekeeping. The efficiency of these control measures is dependent on the degree to which they are performed and the nature of the emission sources.

5.2 Wastewater Treatment

Various forms of wastewater treatment are involved in LNG and SNG plants and refineries. The refinery wastewater treatment procedures will be discussed first because they are the largest and most complete. Many of the techniques and methods used in the refineries will be applicable in the SNG and LNG plant treatment facilities.

The wastewater treatment procedures for the fuel oil refinery and the gasoline refinery are considered together and assumed basically the same. The difference between the two in wastewater sources is the inclusion in the gasoline refinery of sour water from the fluid catalytic cracking unit and the hydrocracker, caustic solution from the Merox treating units, and possible acid wastewater from the alkylation unit. The sour water from the crackers is steam stripped to remove sulfur compounds, ammonia, and phenols. The stripped sour water is then recycled for extraction of the remaining phenols or added directly to the process wastewater stream. Caustic Merox solution poses a special problem as far as pollution. The methods for control of the caustic are discussed later in the report in the section on neutralization of acids and bases. Acid wastewater from the HF alkylation is believed to be no major problem and is merely routed to the process water sewer system.

Methods of treatment and reduction of refinery wastewater are many and quite varied. These methods can be, however, classified into five general categories and they are the following:

1) design of processes providing for lower energy use,

2) elimination of sources of wastewater,

3) design of a segregated wastewater treatment techniques,

4) inplant treatment of wastewater streams, and

5) "tailor-making" of the final process wastewater treatment facilities.

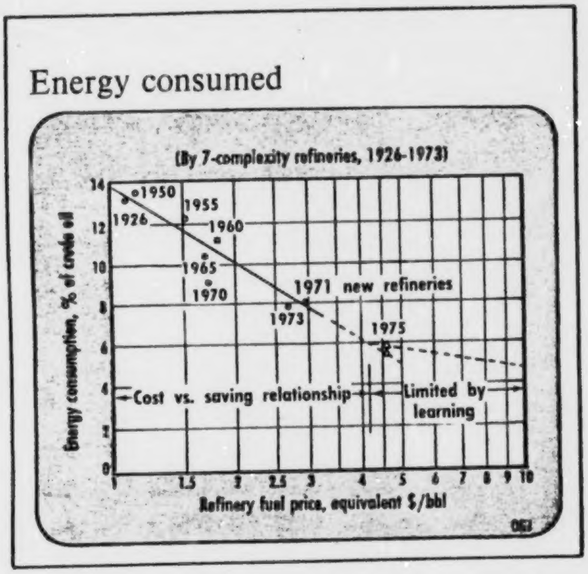
Use of all these methods will produce a high purity final wastewater effluent.

5.2.1 Optimization of Energy Use

Optimizing energy use has always been of concern in refinery design; however, in the last few years the threat of energy shortages has enhanced this concern. Generally speaking a reduction of energy use can be correlated to the reduction of cooling water used within the refinery. Approximately 81% of the water used in a refinery is for cooling and condensing, and about 20% of which is returned as wastewater (TH-038). Figure 5.2-1 shows a continual decline of energy consumption as a percentage of crude oil during the last 25 years which would mean an ultimate decline in wastewater (NE-088). More efficient heat exchange is an excellent method for reducing the total energy consumption. An example of this would be heating a cold process stream with a hot process stream. Discussion of specific areas of heat reduction is beyond the scope of this report.

FIGURE 5.2-1

ENERGY CONSUMPTION IN A REFINERY AS A PERCENTAGE OF CRUDE OIL FOR VARIOUS YEARS



Energy consumed

(By 7-complexity refineries, 1926-1973)

OGJ

5.2.2 Elimination of Wastewater Sources

Elimination of wastewater sources can eliminate many unnecessary pollutants. Many of these methods or procedures are inexpensive and easily adapted. Proper equipment choice will also result in less wastewater produced. Table 5.2-1 gives examples of the correct methods to use to reduce wastewater produced within a refinery (TH-038).

5.2.3 Segregated Wastewater System

A new and very popular idea in refinery wastewater design is a segregated wastewater system. A segregated system has advantages of decreasing the amount of wastewater to be treated and concentrating the pollutants in the wastewater. Typical constituents of a segregated system are given in Table 5.2-2. A flow diagram of the segregated system is shown in Figure 5.2-2 (RA-117).

The clean water system consists of an observation channel or light duty API separator and a large surge basin. Any small amount of oil along with debris is removed in the observation channel. The water in the surge pond can either be routed through the process water treating facility or drained directly to the final holding pond depending on whether it is contaminated or not. Sanitary wastewater can be treated by an inplant bio-treating facility design the same as a municipal wastetreating plant (e.g. activated sludge, chlorination), or if available, may be disposed of directly to a municipal sewer system. If the refinery has docking for tankers, treatment facilities must be provided for the contaminated ballast water. The oily water resulting from ballast is held in a holding tank equipped with floating oil skimmers. Recovered oil is recycled

TABLE 5.2-1

METHODS FOR REDUCING REFINERY WASTEWATER

WRONG METHOD	CORRECT METHOD
1) Use once through cooling water.	1) Recycle cooling water through cooling towers.
2) Use barometric condensers.	2) Use surface condensers.
3) Direct separation of oil-and-water mixtures.	3) Addition of light oil to enhance the separation of oil-and-water separations.
4) Use once through scrubbing.	4) Recycle scrubbing water to scrubber to concentrate pollutants.
5) Use steam vacuum jets.	5) Use a vacuum pump.
6) Use water for cooling.	6) Use air cooling.
7) Use processes producing large amounts of wastewater.	7) Use minimal wastewater producing processes.
8) Desulfurize with water.	8) Hydrodesulfurize.
9) Surface cleanup with water.	9) Surface cleanup with dry or mechanical cleaning devices.

TABLE 5.2-1 METHODS FOR REDUCING REFINERY WASTEWATER (Cont.)

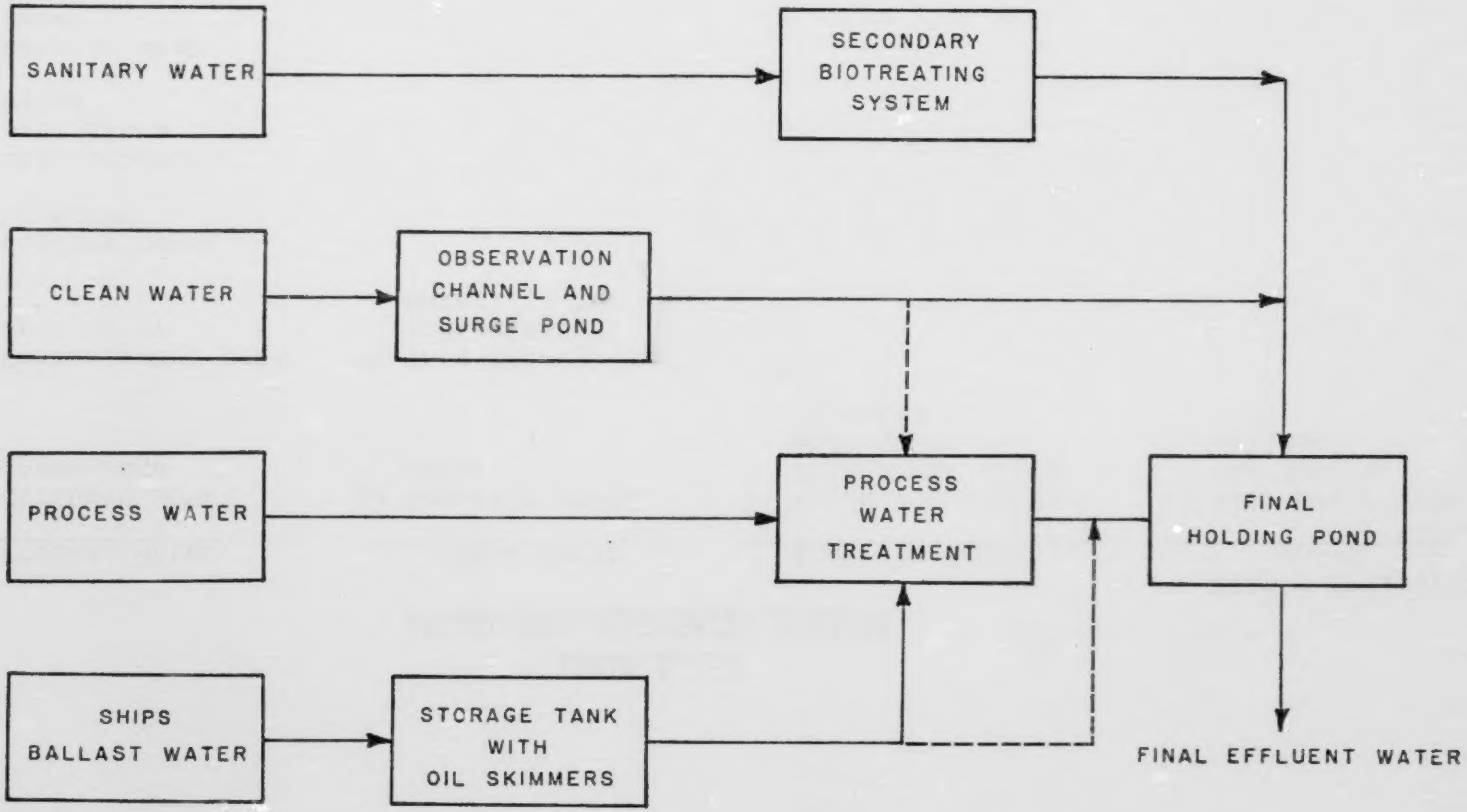
	WRONG METHOD		CORRECT METHOD
10)	Use a water seal on a flare stack.	10)	Use a molecular seal on a flare stack.
11)	Direct steamout or washout of vessels which hold heavy oils.	11)	Flush heavy oil vessels with light oil before steamout or washout.
12)	Dump small amounts of oil to the API separator.	12)	Recover any small amount of oil.
13)	Route pump jacket cooling water to the sewer.	13)	Recycle pump jacket cooling water to the cooling tower.

TABLE 5.2-2

SEGREGATED WASTEWATER STREAMS

Process Water	Clean Water	Sanitary Water	Ship's Ballast Water
1) Stripped sour condensate	1) Non-oily storm water	1) Water and refuse from plant sinks and bathroom fixtures	1) Oily water from the ship's ballast
2) Contaminated process water	2) Once through uncontaminated water		
3) Cooling tower blowdown			
4) Oily process area storm water			
5) Caustic wash water			
6) Oily cleaning water			
7) Desalter water			

FIGURE 5.2-2 TYPICAL SEGREGATED WASTEWATER SYSTEM


SANITARY WATER
SECONDARY BIOTREATING SYSTEM
CLEAN WATER
OBSERVATION CHANNEL AND SURGE POND
PROCESS WATER
PROCESS WATER TREATMENT
FINAL HOLDING POND
SHIPS BALLAST WATER
STORAGE TANK WITH OIL SKIMMERS
FINAL EFFLUENT WATER

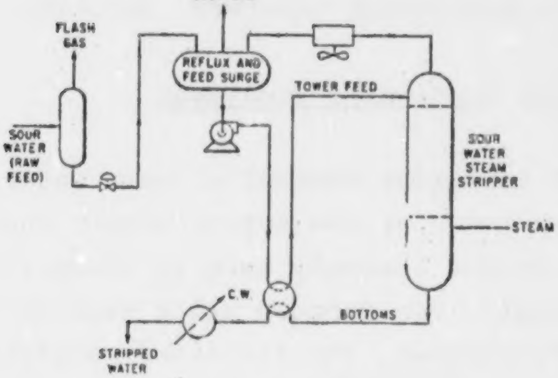
back to the refinery whereas the skimmed water is either introduced to the process water treatment facility or routed to the final holding pond, depending on whether it is or is not contaminated. Treatment of the process water is described in detail later in the report.

Also included in a segregated flow plan is an extensive system known as the "drip system" (GL-027). This system is designed to capture any fugitive oil leaks from pumps, sample lines, and overflows of vessels. The captured oil is returned to the process. The "drip system" will reduce excess oil flowing into the wastewater treatment facility.

5.2.4 Inplant Wastewater Treatment

Water pollution control of wastewater from refinery units can be achieved at the source within the refinery itself. One inplant technique commonly used is steam stripping of sour water or condensate from process units such as the distillation column, the hydrocracker, the fluidized catalytic cracker, and the reforming units. A stripper is operated by blowing steam countercurrently with sour water or condensate in a tray or packed column to remove H_2S, NH_3, and phenol. With efficient steam stripping contaminants removal of 99-100% for H_2S, 95-99% for NH_3, and 50-70% for phenols has been achieved (WA-082). A typical sour water stripper is shown in Figure 5.2-3.

The sour gas must be further processed to separate the H_2S and NH_3. The reasons for the separation are to prevent corrosion and to allow the H_2S to be recovered in the Claus plant. Problems have arisen with corrosion due to ammonium hydrosulfide (NH_4SH). The problems are a result of high concentrations of NH_3 in the H_2S feed to the Claus plant (BR-140). A solution to this problem is use of a "stepped" stripping process where the H_2S is steam stripped in one column while the ammonia is stripped in a second column. This is the basis for the Chevron WWT


SOUR GAS
FLASH GAS
REFLUX AND FEED SURGE
TOWER FEED
SOUR WATER (RAW FEED)
SOUR WATER STEAM STRIPPER
STEAM
C.W.
BOTTOMS
STRIPPED WATER

Typical sour water steam stripper.

FIGURE 5.2-3

process which is shown in Figure 5.2-4. The separation can also be achieved by a DEA absorption process. The H_2S can be recovered as elemental sulfur in the Claus unit. The ammonia can be recovered as pure anhydrous ammonia which is sold or combusted in process heaters.

The stripped water is further treated by another inplant technique, solvent extraction. Foul water containing in excess of 300 ppm of phenols is extracted with either raw or desalted crude oil or light catalytic cycle oil. The effluent water has about 90% of the phenol removed and contains 20 to 30 ppb of oil (WI-142). Extraction with raw crude has the added advantage of desalting the crude with the phenol-laden wastewater. A typical extraction process is shown in Figure 5.2-5 (WI-142).

Oxidization of high sulfide content caustics is another inplant wastewater treatment technique. Sulfidic spent caustics may contain as much as 50,000 ppm of sulfide which is equivalent to a theoretical oxygen demand of 100,000 (BE-147). Spent caustics cannot, however, be steam stripped since sodium sulfide does not hydrolyze to any extent. The alkaline sulfides can be economically oxidized with air to form thiosulfates and sulfates and thus reduce the oxygen demand in the final process wastewater treatment facility. A typical spent caustic oxidizer is shown in Figure 5.2-6 (BE-147).

5.2.5 Process Wastewater Treatment

After having completed all reductions and treatments within the plant the final process wastewater must be treated to meet Federal and local standards of wastewater effluent quality. Refinery process wastewaters are quite varied and sometimes unique, and thus require specific types of treatment.

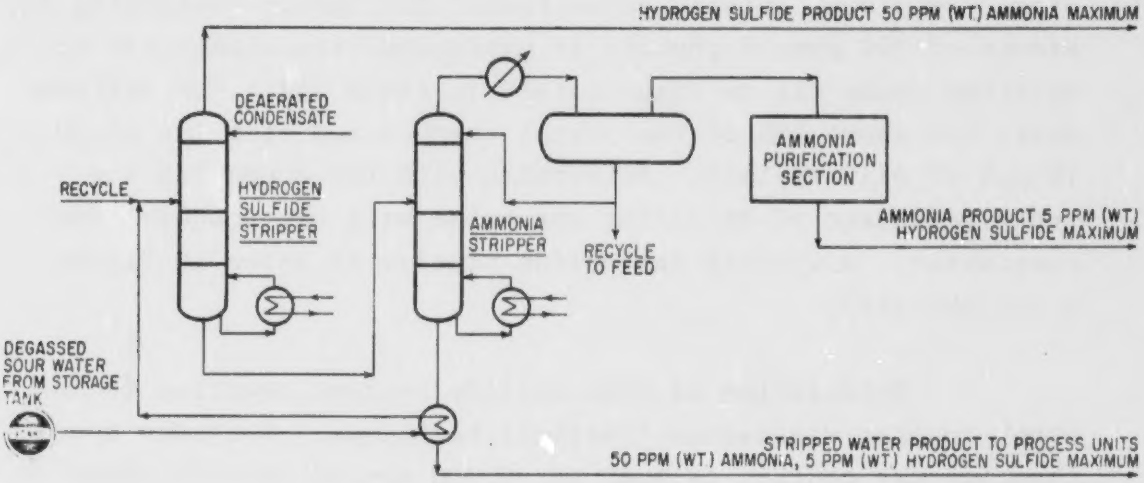

HYDROGEN SULFIDE PRODUCT 50 PPM (WT) AMMONIA MAXIMUM
DEAERATED CONDENSATE
RECYCLE
HYDROGEN SULFIDE STRIPPER
AMMONIA STRIPPER
AMMONIA PURIFICATION SECTION
AMMONIA PRODUCT 5 PPM (WT) HYDROGEN SULFIDE MAXIMUM
RECYCLE TO FEED
DEGASSED SOUR WATER FROM STORAGE TANK
STRIPPED WATER PRODUCT TO PROCESS UNITS
50 PPM (WT) AMMONIA, 5 PPM (WT) HYDROGEN SULFIDE MAXIMUM

FIGURE 5.2-4 CHEVRON WWT PROCESS
Source: KL-032

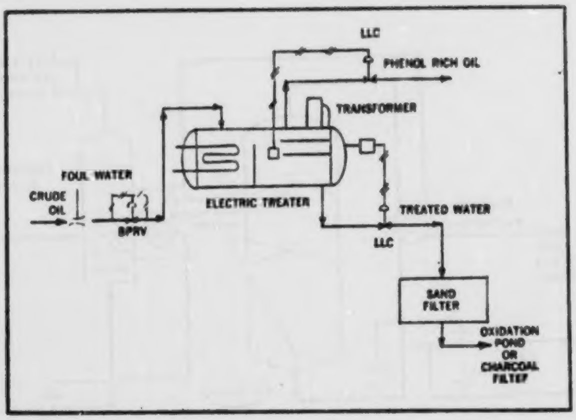
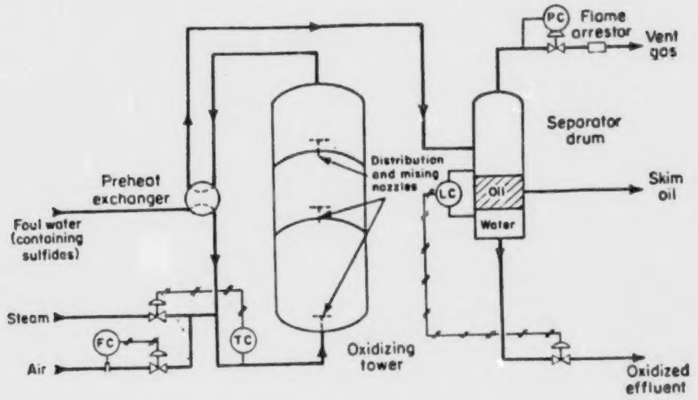

LLC
PHENOL RICH OIL
TRANSFORMER
FOUL WATER
CRUDE OIL
BPRV
ELECTRIC TREATER
TREATED WATER
LLC
SAND FILTER
OXIDATION POND OR CHARCOAL FILTER

FIGURE 5.2-5 EXTRACTION OF PHENOL FROM REFINERY WASTE

FIGURE 5.2-6

TYPICAL OXIDIZING UNIT


PC
Flame arrestor
Vent gas
Separator drum
Distribution and mixing nozzles
Preheat exchanger
LC
Oil
Skim oil
Water
Foul water (containing sulfides)
Steam
FC
TC
Air
Oxidizing tower
Oxidized effluent

Not only the quality of the wastewater to be treated, but also the economical and physical limitations will determine the type of final wastewater treatment facility. The design of a complete "tailor-made" treatment plant has many alternatives. Figure 5.2-7 shows many of the various alternatives open for treatment of refinery wastes.

5.2.5.1 Pretreatment

Generally, the first step in wastewater treatment is referred to as pretreatment. Pretreatment processes will "prepare" the wastewater for further treatment by making the wastewater easier to treat. Pretreatment by aeration and grit removal is completed in an aerated grit chamber. The aeration helps improve the settling characteristics of the solids in the wastes and also improves the odor of the wastewater. This method is not especially designed to handle oily wastewater and, therefore, should probably be used only when the wastewater has a low oil content ($<$100ppm).

For high oil content, wastewater pretreatment can be performed by an API separator, a corrugated plate interceptor, or flocculation. An API separator and a corrugated plate interceptor (CPI) are specifically designed for oil removal. The CPI is based on the theory of oil-water separation which states that the controlling parameter for separation is the surface area per unit flow. The well-designed CPI unit will produce an effluent with a lower oil content than the API separator. The CPI is shown in Figure 5.2-8 (TH-076).

Flocculation is a technique where oil as well as other organic particles within the wastewater are agglomerated by flocculating agents in order to improve their settling characteristics. Two common flocculants are alum and polyelectrolytes which are polar, synthetic, water soluble, organic polymers

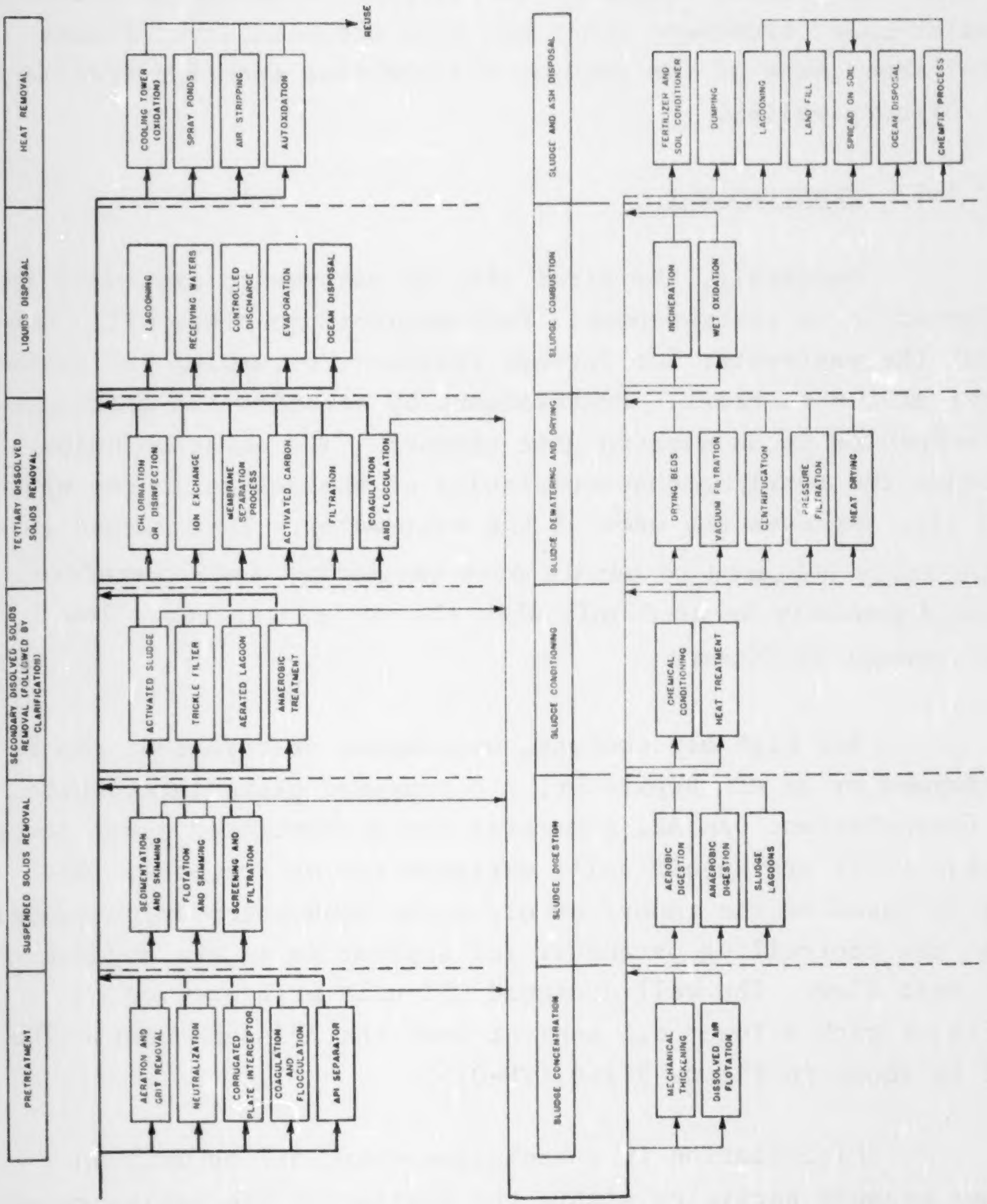

PRETREATMENT
SUSPENDED SOLIDS REMOVAL
SECONDARY DISSOLVED SOLIDS REMOVAL (FOLLOWED BY CLARIFICATION)
TERTIARY DISSOLVED SOLIDS REMOVAL
LIQUIDS DISPOSAL
HEAT REMOVAL
AERATION AND GRIT REMOVAL
NEUTRALIZATION
CORRUGATED PLATE INTERCEPTOR
COAGULATION AND FLOCCULATION
API SEPARATOR
SEDIMENTATION AND SKIMMING
FLOTATION AND SKIMMING
SCREENING AND FILTRATION
ACTIVATED SLUDGE
TRICKLE FILTER
AERATED LAGOON
ANAEROBIC TREATMENT
CHLORINATION OR DISINFECTION
ION EXCHANGE
MEMBRANE SEPARATION PROCESS
ACTIVATED CARBON
FILTRATION
COAGULATION AND FLOCCULATION
LAGOONING
RECEIVING WATERS
CONTROLLED DISCHARGE
EVAPORATION
OCEAN DISPOSAL
COOLING TOWER (OXIDATION)
SPRAY PONDS
AIR STRIPPING
AUTOXIDATION
REUSE
SLUDGE CONCENTRATION
SLUDGE DIGESTION
SLUDGE CONDITIONING
SLUDGE DEWATERING AND DRYING
SLUDGE COMBUSTION
SLUDGE AND ASH DISPOSAL
MECHANICAL THICKENING
DISSOLVED AIR FLOTATION
AEROBIC DIGESTION
ANAEROBIC DIGESTION
SLUDGE LAGOONS
CHEMICAL CONDITIONING
HEAT TREATMENT
DRYING BEDS
VACUUM FILTRATION
CENTRIFUGATION
PRESSURE FILTRATION
HEAT DRYING
INCINERATION
WET OXIDATION
FERTILIZER AND SOIL CONDITIONER
DUMPING
LAGOONING
LAND FILL
SPREAD ON SOIL
OCEAN DISPOSAL
CHEMFIX PROCESS

FIGURE 5.2-7 WASTEWATER PROCESSING ALTERNATIVES FOR A REFINERY

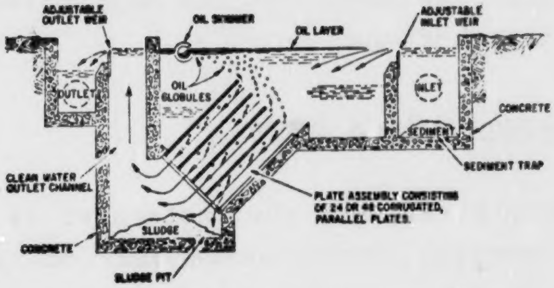

ADJUSTABLE OUTLET WEIR
OIL SKIMMER
OIL LAYER
ADJUSTABLE INLET WEIR
OUTLET
OIL GLOBULES
INLET
CONCRETE
SEDIMENT
SEDIMENT TRAP
CLEAN WATER OUTLET CHANNEL
PLATE ASSEMBLY CONSISTING OF 24 OR 48 CORRUGATED, PARALLEL PLATES.
SLUDGE
CONCRETE
SLUDGE PIT

FIGURE 5.2-8 CORRUGATED PLATE INTERCEPTOR

of high molecular weight (FR-119). While flocculation gives excellent removal of oil and the added advantage of removal of other particulates, it also has higher capital and operating costs than the CPI unit or API unit (BE-147).

If the process wastewater is acidic or basic, it must be neutralized to allow for optimum biological treatment. Various alkali and acid requirements for neutralizing acidic or basic wastewaters is shown in Table 5.2-3 (TE-111). A typical schematic of a batch neutralization is shown in Figure 5.2-9 (BE-147). This would be the treatment used for neutralizing spent Merox treating caustic solutions.

5.2.5.2 Suspended Solids Removal

After pretreatment the wastewater is treated for suspended solids removal. Three common methods are sedimentation, air floatation, and screening and filtration. Sedimentation or gravity settling is no doubt the oldest technique of wastewater treatment. Sedimentation design is based on the settling properties of the wastewater particulates.

Air floatation is a wastewater process where air under pressure (approx. 40 psig) is saturated within the wastewater. When the pressure is released, millions of fine air bubbles less than 100 micron in diameter attach themselves to the particulates in the wastewater and float them to the surface. Where a waste can be treated by either sedimentation or floatation, dissolved-air floatation gives higher separation rates and solids concentration (TE-111). The dissolved air will also enhance the biological oxidation of the waste and the odor characteristics. Air floatation, however, has higher operating costs than sedimentation (BE-147). A dissolved air floatation unit is shown in Figure 5.2-10 (ME-095).

TABLE 5.2-3

NEUTRALIZATION REQUIREMENTS

Alkali Requirements for Acid Neutralization

	Approx. dosage lb./lb. H_2SO_4	Approx. cost cents/lb.*	Neutralization cost cents/lb. H_2SO_4
Dolomitic limestone	0.95	0.2	0.2
High calcium limestone	1.06	0.2	0.2
Dolomitic lime, unslaked	0.53	0.5	0.3
High calcium lime, unslaked	0.60	0.5	0.3
Dolomitic lime, hydrated	0.65	0.6	0.4
High calcium lime, hydrated	0.80	0.6	0.5
Anhydrous ammonia	0.35	4.0	1.4
Soda ash	1.10	1.5	1.6
Caustic soda	0.80	2.5	2.0

* 1968 basis

Acid Requirements for Alkali Neutralization

Acid	Approx. dosage lb./lb. $CaCO_3$	Approx. cost cents/lb.*	Neutralization cost cents/lb. $CaCO_3$
H_2SO_4, 66°Be	1.0	1.5	1.5
HCl, 20°Be	2.0	1.5	3.0
Flue gas, 15% CO_2	3.0	(1)	—
Sulfur (2)	0.3	2.0	0.6

(1) Cost would be based on blower design and equipment amortization.

(2) The use of sulfur would produce a reducing condition which might require additional treatment to produce an oxygen-containing effluent.

* 1968 basis

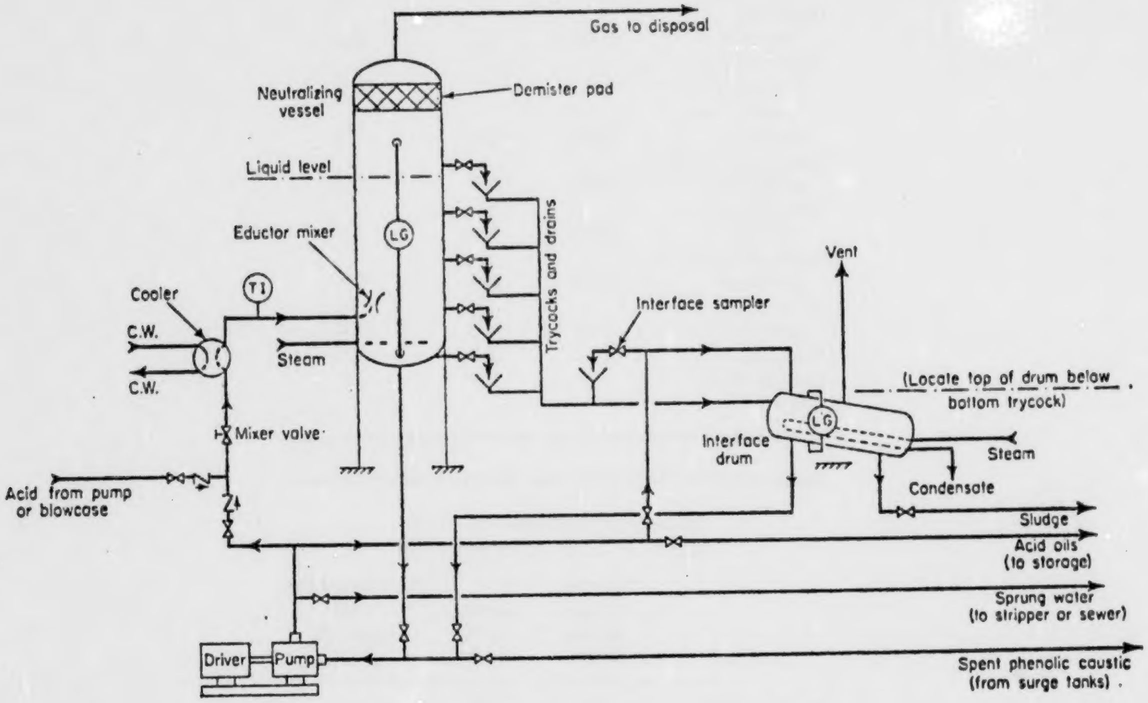

Gas to disposal
Neutralizing vessel
Demister pad
Liquid level
LG
Eductor mixer
Trycocks and drains
Vent
TI
Cooler
C.W.
C.W.
Steam
Interface sampler
(Locate top of drum below bottom trycock)
LG
Interface drum
Steam
Mixer valve
Condensate
Acid from pump or blowcase
Sludge
Acid oils (to storage)
Sprung water (to stripper or sewer)
Driver
Pump
Spent phenolic caustic (from surge tanks)

FIGURE 5.2-9 BATCH NEUTRALIZATION OF SPENT CAUSTIC WITH ACID

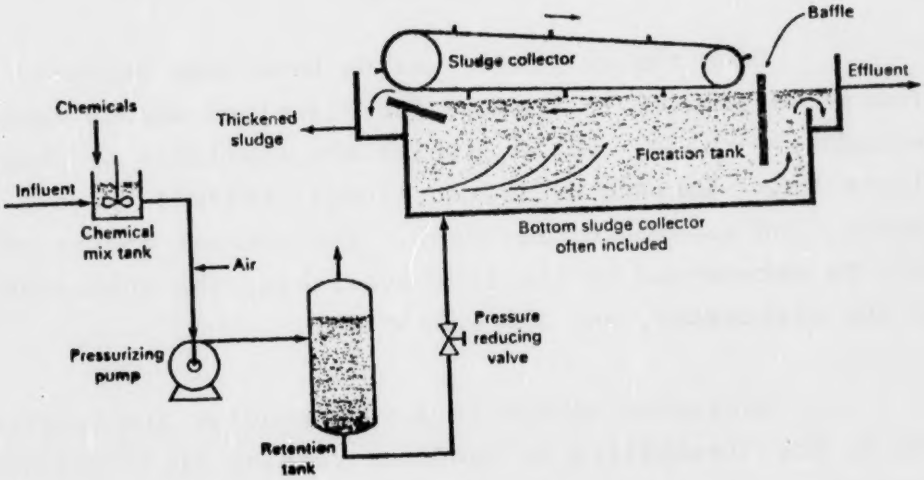

Baffle
Sludge collector
Effluent
Chemicals
Thickened sludge
Flotation tank
Influent
Chemical mix tank
Bottom sludge collector often included
Air
Pressure reducing valve
Pressurizing pump
Retention tank

FIGURE 5.2-10 SCHEMATIC OF DISSOLVED-AIR FLOATATION TANK WITHOUT RECYCLE

Generally screening and filtration should be used for suspended solids removal when the wastewater has a small solids loading and when one desires a high degree of separation. Under high solids loadings the economics will suggest a sedimentation unit or floatation unit. The wastewater effluent from the suspended solids removal unit is on the order of 5-20 ppm of oil and 25-60 ppm of suspended solids (BE-156).

5.2.5.3 Dissolved Solids Removal

Once the suspended solids have been removed, the process wastewater is treated for dissolved solids removal by secondary methods. Options which are available as shown in Figure 5.2-7 include activated sludge, trickle filter, aerated lagoon, and anaerobic treatment. The correct choice of process will be determined by the land available, the characteristics of the wastewater, and the economics.

Activated sludge is a very popular bio-treating process due to its flexibility in handling varying dissolved solids loading and wastewater flow rates. A conventional activated sludge process consists of an aeration tank, a secondary clarifier, and a sludge recycle system. Wastewater enters the aeration tank along with recycle sludge and contacts with dissolved air which promotes biological oxidation of the dissolved organics. The oxidized sludge is settled out in a clarifier. Part of the sludge is recycled back to the aeration tank and the remaining sludge is wasted to the sludge treating facility. A conventional activated sludge system is shown in Figure 5.2-11 (ME-095). The BOD removal efficiencies and the applications of the conventional activated sludge process and various process modifications are shown in Table 5.2-4 (ME-095). The activated sludge process has the advantages over trickle filter or aerated lagoon of a smaller land requirement and a more convenient sludge handling system.

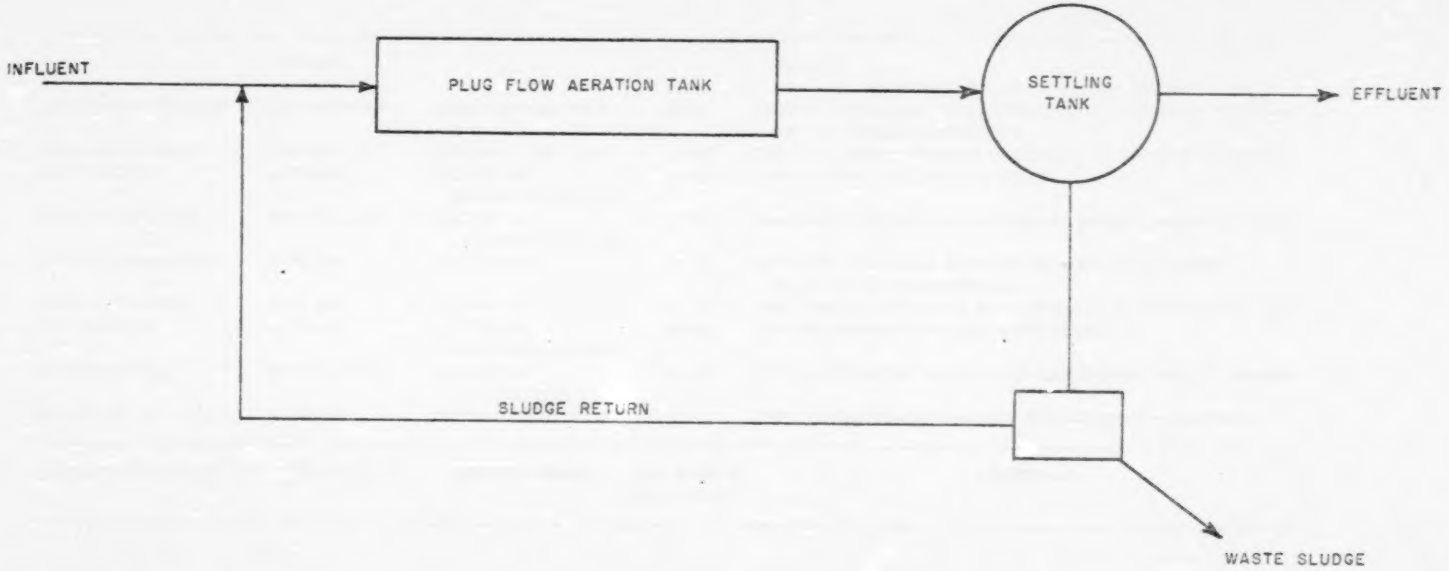

INFLUENT
PLUG FLOW AERATION TANK
SETTLING TANK
EFFLUENT
SLUDGE RETURN
WASTE SLUDGE

FIGURE 5.2-11 CONVENTIONAL ACTIVATED SLUDGE PROCESS

TABLE 5.2-4

OPERATIONAL CHARACTERISTICS OF ACTIVATED-SLUDGE PROCESSES

Process modification	Flow model	Aeration system	BOD removal efficiency, %	Application
Conventional	Plug-flow	Diffused-air, mechanical aerators	85–95	Low-strength domestic wastes, susceptible to shock loads
Complete-mix	Complete-mix	Diffused-air, mechanical aerators	85–95	General application, resistant to shock loads, surface aerators
Step-aeration	Plug-flow	Diffused-air	85–95	General application to wide range of wastes
Modified-aeration	Plug-flow	Diffused-air	60–75	Intermediate degree of treatment where cell tissue in the effluent is not objectionable
Contact-stabilization	Plug-flow	Diffused-air, mechanical aerators	80–90	Expansion of existing systems, package plants, flexible
Extended-aeration	Complete-mix	Diffused-air, mechanical aerators	75–95	Small communities, package plants, flexible, surface aerators
Kraus process	Plug-flow	Diffused-air	85–95	Low-nitrogen, high-strength wastes
High-rate aeration	Complete-mix	Mechanical aerators	75–90	Use with turbine aerators to transfer oxygen and control the floc size, general application
Pure-oxygen systems	Complete-mix reactors in series	Mechanical aerators	85–95	General application, use where limited volume is available, use near economical source of oxygen, turbine or surface aerators

The aerated lagoon is a very popular technique for biological treatment of refinery process wastewater (PR-046). The aerated lagoon is a basin where wastewater is biologically treated by oxidation. Oxygen is supplied by means of surface aerators or diffused aeration units (ME-095). Aerated lagoons can either be run on a once through basis or with a recycle. Disadvantages with the process are a large land requirement and difficulty in sludge handling.

The trickling filter is another alternative for secondary removal of dissolved solids. Trickling filters consist of a bed of rock or other packing material which can support a biological growth. The wastewater is distributed over the bed and allowed to "trickle" through the voids contacting with the supported biomass. Trickling filters are classified by hydraulic or organic loading as high-rate or low-rate. A comparison of the two is shown in Table 5.2-5 (ME-095). An improvement in the trickling filter is the use of a fabricated polyvinyl chloride packing instead of rock for greater BOD loadings (TE-111). An alternative trickling filter process is Allis-Chalmers Bio-Disc process in which micro-organisms grow on rotating discs that are partially submerged in the wastewater. The company reports BOD loadings of 600 lb per 1,000 cubic feet and BOD removal of 90% for raw wastes containing 1,000 mg/liter of dissolved organics (TE-111). Disadvantages of the trickling filter are large land use, difficulty in sludge handling, and production of offensive odors (ME-095).

All aeration processes can experience a size (or land area) reduction when pure oxygen is used instead of air. Also, most industrial effluents are considerably stronger than sanitary wastes, and thus, demand a high oxygen uptake rate during biological treatment. Further, variations in theoretical oxygen

TABLE 5.2-5

COMPARISON OF LOW-RATE AND HIGH-RATE TRICKLING FILTERS

Factor	Low-rate filter	High-rate filter
Hydraulic loading, mgad	1 to 4	10 to 40
Organic loading, lb BOD_5/acre-ft-day	300 to 1,000	1,000 to 5,000
Depth, ft	6 to 10	3 to 8
Recirculation	None	1:1 to 4:1
Rock volume	5 to 10 times	1
Power requirements	None	10 to 50 hp/mg
Filter flies	Many	Few, larvae are washed away
Sloughing	Intermittent	Continuous
Operation	Simple	Some skill
Dosing interval	Not more than 5 min (generally intermittent)	Not more than 15 sec (continuous)
Effluent	Fully nitrified	Nitrification at low loadings

demand fluctuate greater in industrial wastewater than municipal wastewater due to the fact that spills or upsets are immediately felt at the treatment facility and are not generally diluted. The economics will, however, determine the feasibility of the use of pure oxygen in bio-treating.

Anaerobic treatment processes such as stabilization ponds can be used to treat refinery wastewater but are not used frequently because concentrations of organic material are generally low and because of the types of compounds present. Also, the anaerobic process gives off H_2S as a result of decomposition of sulfurous material in the wastewater, which results in an odor problem (AM-062, ME-095).

A comparison of all the above four biological treatment process as far as area requirement, BOD loading, and BOD removal is given in Table 5.2-6 (TE-111).

5.2.5.4 Tertiary Dissolved Solids Removal or Treatment

To further improve the quality of the wastewater effluent, processes defined as tertiary processes can be used for removal of special troublesome pollutants. Presently, tertiary processes are not a vital part of a treatment facility; however, in the future with stricter wastewater effluent standards tertiary treatment will probably become a basic unit of the wastewater treatment facility. As shown in Figure 5.2-7, the tertiary processes considered for refinery wastewater are chlorination, ion exchange, membrane separation processes, activated carbon, filtration, and coagulation and floatation.

TABLE 5.2-6

COMPARISON OF BIOLOGICAL PROCESSES -

Requirements to treat 1,700 lb. BOD/day

	Area, acres	Biological loading lb. BOD/ 1,000 cu. ft.	BOD removal, %
Stabilization pond	57[1]	0.09 to 0.23	70 to 90
Aerated lagoon	5.75[2]	1.15 to 1.60	80 to 90
Activated sludge			
Extended	0.23	11.0 to 30.0	95+
Conventional	0.08	33.0 to 400	90
High rate	0.046	57.0 to 150	70
Trickling filter			
Rock	0.2 to 0.5	0.7 to 50	40 to 70
Plastic media	0.02 to 0.08	20 to 200	50 to 70

(1) 5-ft. deep (2) 10-ft. deep

Chlorination is probably the most commonly used process today for final chemical treatment of wastewater. Chlorine compounds used include calcium hypochlorite, sodium hypochlorite, and pure chlorine. The former two are generally used in smaller wastewater treatment facility or for safety reasons. Common dosages of chlorine for various wastewaters are shown in Table 5.2-7 (ME-095).

Ion exchange as a tertiary technique is used for the removal of inorganic ions or nutrients from the wastewater. Three common nutrients removed by ion exchange are nitrates, phosphates, and ammonia. Pilot plant operations have shown 70 percent removal of phosphates, 90 percent removel of nitrates, and 93-97 percent removal of ammonia (CU-008). Zeolite is the main ion exchange resin employed. Ion exchange is also used in the demineralization of boiler water feeds. Ion exchange has also been mentioned as a possible secondary method for the removal of organics from the wastewater. Resin regeneration and plugging have, however, been major problems in this type of removal (CU-008). Another possible use of ion exchange is in the recovery of chromates (CrO_4) from cooling tower blowdowns. The chromates are used as corrosion inhibitors and can be economically recovered by ion exchange (BE-156).

New and diversified methods of tertiary treatment of refinery process wastewater for removal of very small particulates are membrane separation processes. The typical membrane process uses a semipermeable-type membrane to concentrate various components of the wastewater stream. Variations in the driving forces used and the degree of separation define the specific membrane process. Examples of membrane processes are electrodialysis reverse osmosis, ultrafiltration, and microfiltration. The useful size ranges of particulates which can be removed are illustrated in Figure 5.2-12 (LA-150). Reverse osmosis is the only membrane process which has been used commercially in the treatment of municipal wastewater.

TABLE 5.2-7

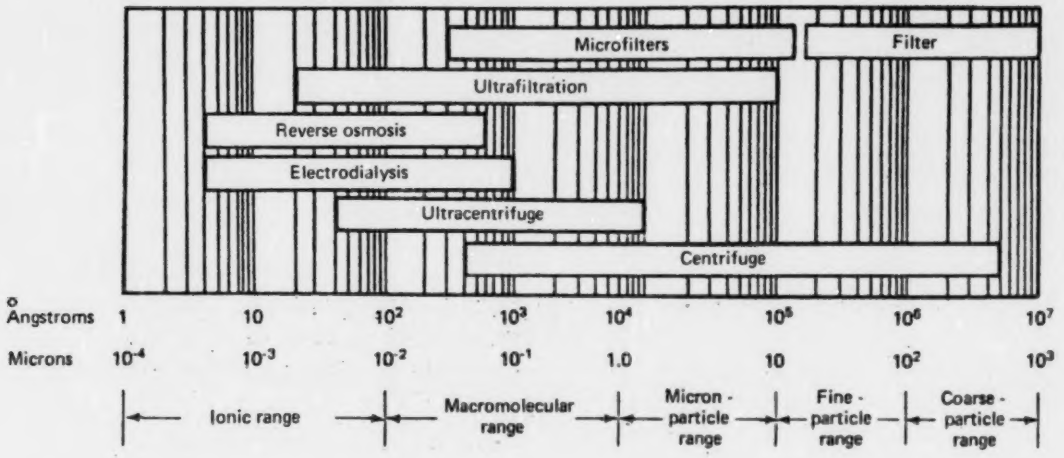
CHLORINATION APPLICATIONS IN WASTEWATER COLLECTION, TREATMENT, AND DISPOSAL

Application	Dosage range, mg/liter	Remarks
Collection:		
Slime-growth control	1–10	Control of fungi and slime-producing bacteria
Corrosion control (H_2S)	2–9*	Control brought about by destruction of H_2S in sewers
Odor control	2–9*	Especially in pump stations and long flat sewers
Treatment:		
Grease removal	2–10	Added before preaeration
BOD reduction	0.5–2†	Oxidation of organic substances
Ferrous sulfate oxidation	‡	Production of ferric sulfate and ferric chloride
Filter-ponding control	1–10	Residual at filter nozzles
Filter-fly control	0.1–0.5	Residual at filter nozzles, used during fly season
Sludge-bulking control	1–10	Temporary control measure
Digester supernatant oxidation	20–140	
Digester and Imhoff tank foaming control	2–15	
Nitrate reduction	See Chap. 14	Conversion of nitrate to ammonia
Disposal:		
Bacterial reduction	2–20	Plant overflows, storm water
Disinfection	See Table 11·8	Depends on nature of wastewater

* Per mg/liter of H_2S.
† Per mg/liter of BOD_5 destroyed.
‡ $6FeSO_4 \cdot 7H_2O + 3Cl_2 \rightarrow 2FeCl_3 + 2Fe_2(SO_4)_3 + 42H_2O$.

FIGURE 5.2-12

USEFUL RANGES OF SEPARATION PROCESSES



In reverse osmosis, membranes allow passage of water and/or hydrogen bonding solvents but impede the passage of salts and small molecules. Pressure is applied to the "polluted" wastewater stream to overcome the osmotic pressure and force water through the membrane. Possible uses in the refinery are treatment of cooling tower blowdown, boiler water blowdown, wastewater treatment plant rinses, paved utility area drain water, clean storm water, desalter water, API separator effluent, and selected tank bottom water draw-offs (NE-087). Major disadvantages of reverse osmosis are: (1) the present availability of only a few membranes such as cellulose acetate and aromatic polyamide which will limit operating conditions and treatable wastewater, (2) fouling of membranes due to high solids loading, and (3) concentrated solutions which exert an osmotic pressure so great that it would be uneconomical to treat (NU-009, LE-148).

Activated carbon is a very promising and flexible method of tertiary treatment. The activated carbon acts as a molecular trap where molecules can diffuse in but are then slowed down within the carbon matrix. Large surface to volume ratios (450 to 1,800 square meters/gm) indicate the complex structure of the carbon (HU-094). The trapped molecules are either thrown away with the activated carbon or regenerated by oxidation or desorption. As a tertiary treatment process, activated carbon can remove as much as 95 percent of the dissolved organics from a typical industrial wastewater (BE-156).

Filtration can also be used as a tertiary treatment. Types of filters currently used in wastewater treatment include slow and rapid sand filters, multi-media filters, and moving bed filters (MBF).

Microfiltration or microstrainers can be used to remove particles in the 10 micron to 10^{-2} micron range (Figure 5.2-12). Filtration of this type is performed on a variable, low-speed rotating drum. The degree of separation will depend on the solids loading and the filter media.

Slow sand filters consist of a 6 to 15 inch layer of sand which is placed over a layer of coarser material of similar thickness, and also a drainage system. When in service, the filters give about 60 percent removal of suspended solids and 40 percent removal of BOD at hydraulic loading rates of 1.5-2.5 gal/ft^2/hr (CU-008). Disadvantages of the system are moderate performance at best, large area requirement, and high maintenance costs. Rapid sand filters are constructed much the same as the slow sand filters, but are designed for loading in the range of 2-6 gpm/ft^2. Under these loadings and with the use of coagulants removal of suspended solids is approximately 70 percent and of BOD 80 percent (CU-008). Slow or rapid sand filtration can be used for tertiary treatment of wastewater but are generally not recommended due to the fact that multi-media filtration gives better separation and is approximately equal in costs.

Multi-media is the recommended tertiary sand filter treatment in that it gives "in-depth" filtration of the sludge. "In-depth" filtration is the filtering of wastewater within the sand filter and not just filtration on the surface as with slow or rapid single component sand filters. Some dual medium filter beds which have been used in treating wastewater are (1) anthracite and sand, (2) activated carbon and sand, (3) resin beds and sand, and (4) resin beds and anthracite (ME-095). Multi-medium filters that show promise are composed of (1) anthracite, sand, and garnet; (2) activated carbon, anthracite, and sand; (3) weighted spherical resin beads (charged and uncharged), anthracite, and sand; and (4) activated carbon, sand, and garnet (ME-095). Multi-media filtration can tolerate higher suspended solids loadings than the single component sand filter.

The moving bed filter is a new method of applying sand filtration that is being applied by Johns-Manville Products Corporation (CU-008). A sand filter bed is moved countercurrently to incoming wastewater by means of a hydraulically activated diaphram. The sand is cleaned in a wash tower and recycled back to the sand filter. The continuous operation means no stopping for backwashing as in a conventional unit. In pilot plant operation and using coagulation prior to filtering BOD was reduced from 40-64 mg/l to 8.8-10.0 mg/l, COD from 111-172 mg/l to 39-43 mg/l, and total phosphate from 30-40 mg/l to 1.5-2.5 mg/l (CU-008).

Coagulation and flocculation have also been used a tertiary removal technique. The American Oil Company has adapted this method whereas previously other installations in the petroleum industry have used chemical coagulation plus air floatation as a secondary treatment after primary gravity settling and before bio-oxidation pond (FR-119). Typical coagulants used are alum ($Al_2(SO_4)_3 \cdot 14H_2O$), sodium aluminate ($NaAlO_2$), ferrous sulphate ($FeSO_4$), ferric chloride ($FeCl_3$), lime ($CaO$), and polyelectrolytes. The flocculation-air floatation tertiary treatment results in removals of 70-85 percent of the oil, 30-50 percent of suspended solids, 45-55 percent of the 5-day BOD, and 70-85 percent of phosphates (FR-119).

5.2.5.5 Final Liquids Disposal

The final liquids disposal should be of no real problem if the quality of the effluent is within the standards. Methods of disposal include direct discharge into the receiving waters or into the ocean, controlled discharge from a holding pond, or eventual discharge from a series of lagoons (lagooning). If for some reason discharging is not feasible, zero discharge can be accomplished through evaporation ponds. This method is very valuable in arid climates.

To cut back the wastewater discharge to the environment, the treated wastewater can be further purified to allow for its eventual reuse in the refinery. These processes are oxidation-type processes where the wastewater effluent is saturated with oxygen from air. This final oxidation is for removal of hard to oxidize components such as phenol, nitrates, and ammonia. Further treating will also include heat removal from the wastewater stream. Examples of the cooling-oxidation processes are spray ponds, air stripping, autoxidation, and cooling towers.

Spray ponds or lagoons are holding ponds with some type of aeration system (the same design as aerated lagoons). The spray pond will have a lower oxygen demand but require a long retention time for oxidation of nitrates (ME-095).

Air stripping is a process which has been successful in the removal of ammonia from wastewater streams. The theory is based on the equilibrium as shown in the following equation:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

As the wastewater is made more basic, the equilibrium is shifted to more NH_3 which is stripped by air (ME-095). The stripping is performed in a packed column by countercurrent contact of the air and gas. Air stripping has also been performed on raw sewage. Stripping will remove lighter hydrocarbons but heavier organics will stay in the water.

Autoxidation uses an oxidation-aeration tower and takes advantage of stripping and cooling actions as well as oxidation. The process removes residual hydrocarbons catalytically by radical addition to form a hydroperoxide and subsequent decomposition of the peroxide (PR-046). Contacting is done in an aeration tower containing the radical forming catalyst. Cobalt, nickel, chromium, and iron have been reported as catalysts (PR-046).

A final oxidation and cooling method is by means of a cooling tower. Organic wastes and other pollutants such as heavy metals are removed through a combination of biodegradation, precipitation, sorption, and volatilization (GL-027). Normally one would expect fouling of heat exchange equipment by biological or inorganic materials from the cooling tower water. This, however, does not occur and is believed due to the abnormally large amount of heavy metals within the cooling water. If slime growths are a problem increased chlorination and the occasional use of dispersants is recommended (HA-132). The biological sludge is removed from the bottom of the cooling tower and disposed of through incineration or landfill. Expected reduction in pollutants from a cooling tower are shown in Table 5.2-8 (HA-132).

5.2.5.6 Sludge Handling

Sludge from a refinery wastewater are of two kinds; oily and biological. The oily sludges results from the API separator or the CPI unit treatment of the wastewater, stable emulsions from tank bottoms, and also from skimming operations in the ship's ballast water holding tank, primary sedimentation, and air floatation, and also minor amounts from the clean water observation channel. For several years refiners have disposed of oily sludge through a special landfilling technique. This technique, however, requires on the order of seven acres of land and is not effective if soil conditions allow contamination of underground water supplies (CH-196). Incineration of oily wastes has many advantages and is sometimes the only solution. Incineration is discussed in the following section on solid waste disposal. Another alternative would be to recycle the oil back into the refinery. This method requires additional

TABLE 5.2-8

EXPECTED POLLUTION REDUCTION FROM COOLING TOWER TREATMENT

Pollutant	Percent Reduction
Oil	60
Phenols	80
Ammonia-nitrogen	60
BOD	60
Suspended Solids	50

oil-water separation equipment. As the value of hydrocarbons increases, this method of removal may become economically feasible.

Biological sludges resulting from sedimentation and bio-treating are collected in sedimentation tanks, flocculation units, screens, filters, and clarifiers. The steps involved in sludge handling before sludge combustion and final disposal are shown in Figure 5.2-7 (Pg. 292) and include concentration, digestion, conditioning, and dewatering and drying. Total solids in the raw sludge range from 2 to 7% with a typical sludge being 4% (ME-095).

Sludge concentration processes include gravity or mechanical thickening and dissolved air floatation. A mechanical thickener is designed on the same principles as sedimentation. A solids concentration of 5 to 6% can result from mechanical thickening. A typical mechanical thickener is shown in Figure 5.2-13 (ME-095). Floatation thickeners are the same design as the thickener described earlier for suspended solids removal (Figure 5.2-10, Pg. 297). Concentration of the sludge ranges from 4 to 8%. Concentration will be aided by the addition of polyelectrolytes (ME-095).

Sludge digestion can be completed by either aerobic or anaerobic methods. Anaerobic digestion of biological sludges from refineries is rarely done even though there may be some value in it. Anaerobic treatment can be only justified economically for large installations (AM-062). Design of an anaerobic digester for a refinery would be the same as for a municipal wastewater treating facility.

Aerobic digestion of sludge usually results from extended aeration, contact stabilization, or aeration in lagoons with large retention times. The advantage of aerobic digestion over anaerobic are:

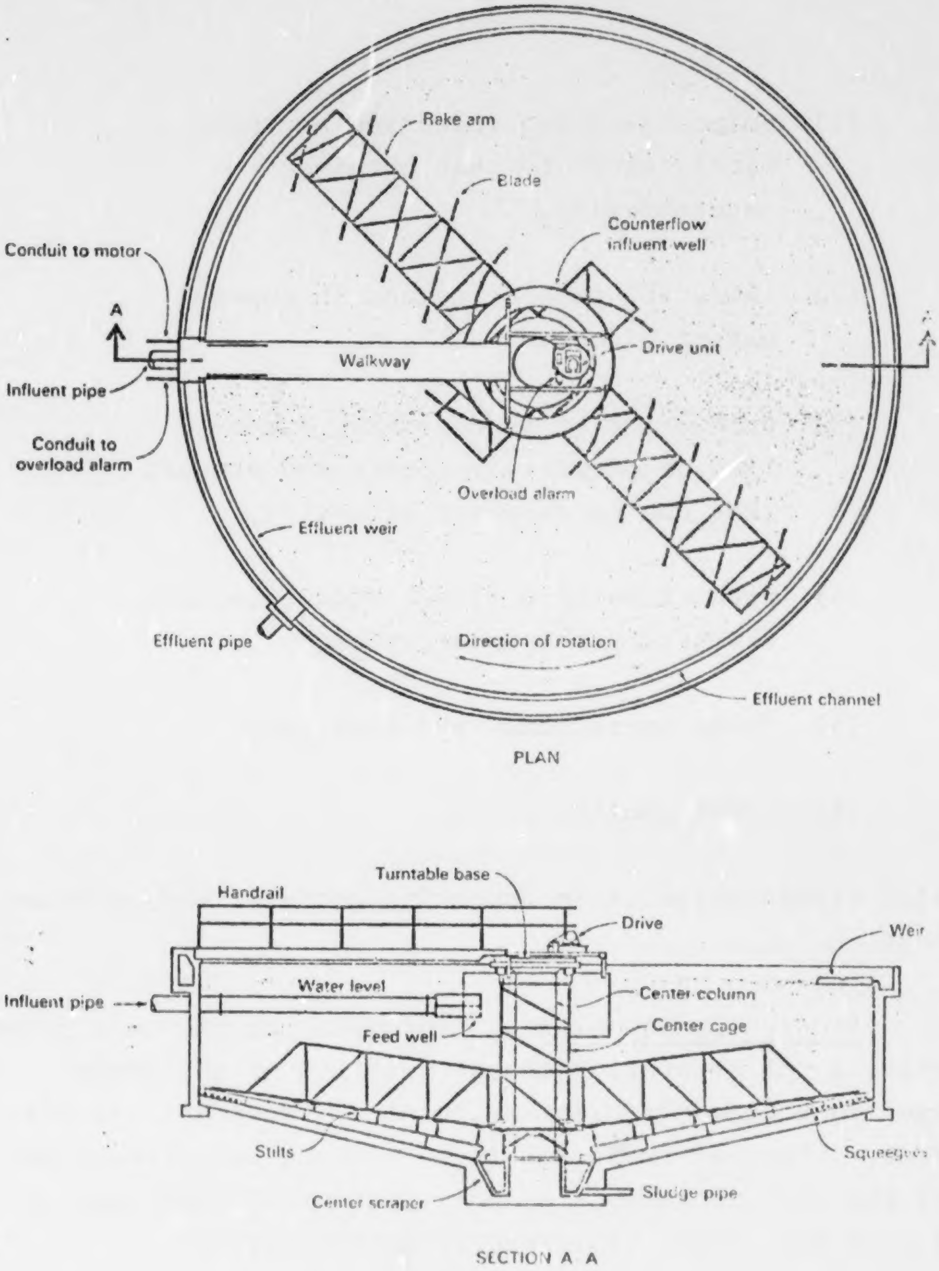

Rake arm
Blade
Counterflow influent well
Conduit to motor
A
Walkway
Drive unit
A
Influent pipe
Conduit to overload alarm
Overload alarm
Effluent weir
Effluent pipe
Direction of rotation
Effluent channel
PLAN
Turntable base
Handrail
Drive
Weir
Water level
Influent pipe
Center column
Center cage
Feed well
Stilts
Squeegees
Center scraper
Sludge pipe
SECTION A A

FIGURE 5.2-13 SCHEMATIC OF A MECHANICAL THICKENER (FROM DORR-OLIVER)

(1) volatile-solids reduction approximately equal to that obtained anaerobically,

(2) lower BOD concentrations in supernatant liquor,

(3) production of an odorless, humus-like, biologically stable end product that can be disposed of easily,

(4) production of a sludge with excellent dewatering characteristics,

(5) fewer operational problems, and

(6) lower capital costs.

The major disadvantage is in operating costs of the aeration equipment.

Sludge conditioning is preformed for the sole purpose of improving the dewatering characteristics of the sludge. The two types most commonly used are chemical treatment and heat treatment. Chemical treatment is in essence coagulation and employs the same coagulants as previously mentioned such as ferric chloride, lime, alum, and polyelectrolytes.

Heating the sludge for short periods of time under pressure will result in coagulation of solids, breakdown of the gel structure, and a reduction in the affinity of the solids for water. Additional advantages are near sterilization and deodorization of the sludge. The supernatant from heat treated sludge is high in concentration of low molecular weight, highly soluble organic compounds. These compounds are easy to biologically treat and should be returned to the biological treating area of waste disposal plant.

Other techniques investigated for sludge conditioning are freezing and irradiation (ME-095). Much research needs to be done, however, to make these processes feasible or economical.

Sludge drying and dewatering is made easier once the sludge has been conditioned. Dewatering and drying processes include drying beds, vacuum filtration, centrifugation, pressure filtration, and heat drying. The choice among this method will depend on the characteristics of the sludge, the land available, the method of final sludge disposal, and the economics of the situation.

Drying beds are used to dewater digested sludge. The total number of beds will be determined by the digested sludge production rate and the moisture content desired in the sludge. Each bed is designed to hold approximately one-half to one load from a digester. The beds are sand and include an underground drainage system to drain water. If odor is a problem, the beds can be covered with green-house types of enclosures. Under favorable conditions a 10 to 15 day retention time will result in a sludge containing 60% water (ME-095). Drying beds will require a large land area.

Vacuum filtration is probably the most widely employed mechanical means of dewatering sludges. There are many vacuum filters which can be applied to dewatering sludge. In selecting a filter, important factors to consider are the following: (1) sludge slurry character, (2) sludge production level, (3) required results, and (4) materials of construction. The most common type of vacuum filter is the rotary drum. There are variations in the rotary drum such as multicompartment, single-compartment, belt, precoat, Dorrco, hopper dewaters, and top feed. A typical continious rotary drum filtration process is shown in Figure 5.2-14 (CH-196). Other types of vacuum filters include scroll-discharge, tilting-pan, disk, and batch leaf. Moisture content of a vacuum filtered sludge usually is on the order of 70 to 80 percent; however, filters may be operated to produce a cake of 60 to 70 percent if desired (ME-095).

Centrifugation can also be used to dewater refinery process wastewater sludges. The commonly used sewage treatment centrifuge is the solid-bowl type. The moisture content of the sludge cake produced is 75 to 80 percent (ME-095). One major drawback of centrifuging is disposal of the centrate which is relatively high in suspended, nonsettling solids. Recycle of the centrate back into the wastewater treating facility could result in a large solids loading. Two methods to help eliminate this problem are (1) design of a longer liquid retention time in the centrifuge and (2) use of coagulating agents (ME-095). The scroll-discharge centrifuge is another type centrifuge that could possibly be employed in dewatering wastewater sludges.

Pressure filtration is preformed by a filter press consisting of a series of filter cloth-fitted, rectangular plates supported face to face. The plates are held together by a pressure sufficient to seal them to withstand the pressure applied during the filtration processes. The moisture content of the cake produced is 55 to 70 percent (ME-095). The filter press is capable of handling most any type of sludge and has the advantage of producing a filtrate which contains 10-20 mg/l of suspended solids and less than 200 mg/l BOD (CU-008). Conditioning of the sludge may or may not be needed. A typical filter press operation is shown in Figure 5.2-15 (CU-008).

FIGURE 5.2-14

FLOWSHEET OF CONTINUOUS VACUUM FILTRATION

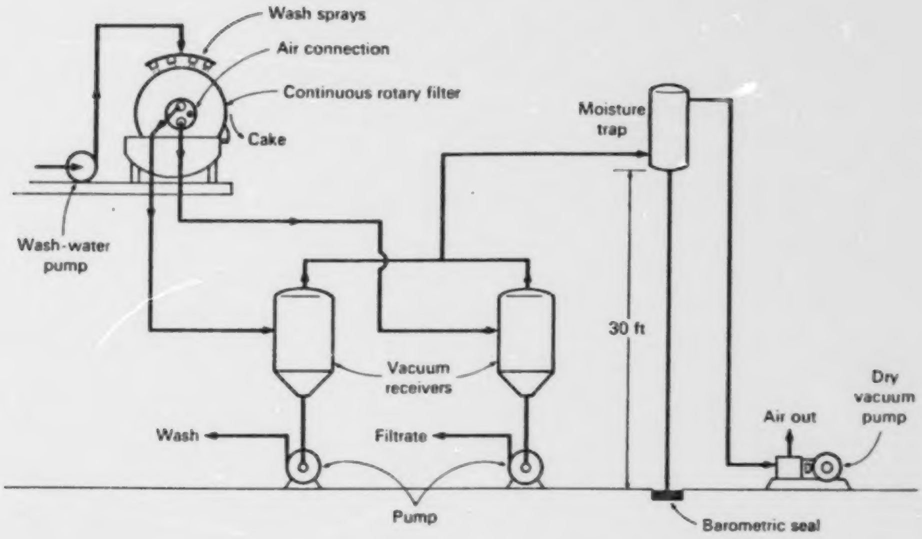
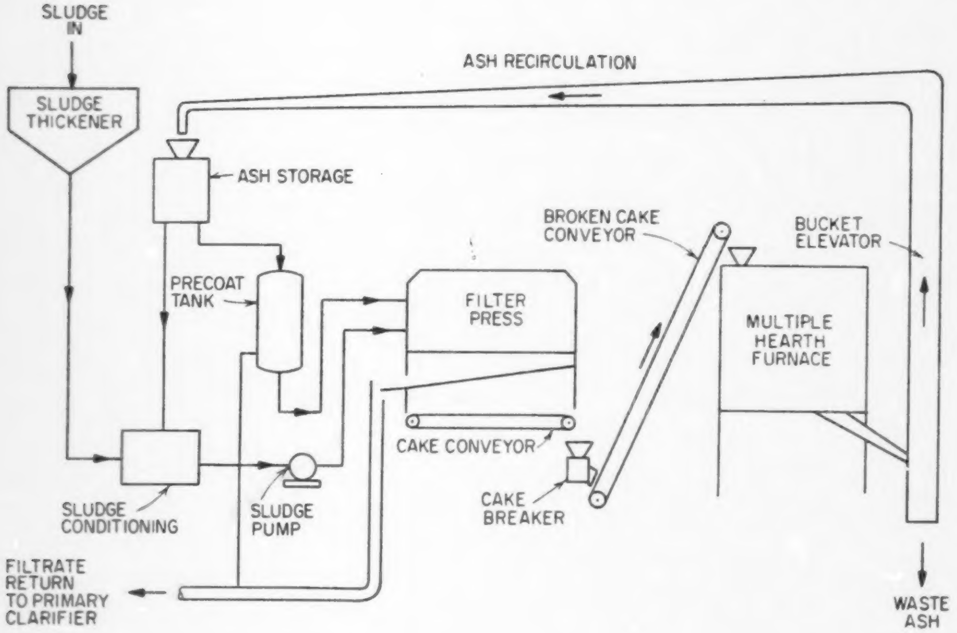

Wash sprays
Air connection
Continuous rotary filter
Cake
Wash-water pump
Moisture trap
30 ft
Vacuum receivers
Wash
Filtrate
Pump
Air out
Dry vacuum pump
Barometric seal

FIGURE 5.2-15

PASSAVANT FILTER SLUDGE DEWATERING SYSTEM
(COURTESY OF PASSAVANT CO.)


SLUDGE IN
ASH RECIRCULATION
SLUDGE THICKENER
ASH STORAGE
BROKEN CAKE CONVEYOR
BUCKET ELEVATOR
PRECOAT TANK
FILTER PRESS
MULTIPLE HEARTH FURNACE
CAKE CONVEYOR
CAKE BREAKER
SLUDGE CONDITIONING
SLUDGE PUMP
FILTRATE RETURN TO PRIMARY CLARIFIER
WASTE ASH

Heat drying may also be used to dewater sludges and has been used to dry sludges for more efficient incineration or processing into fertilizer. The drying is most commonly preformed in the C. E. Raymond Flash Drying System (Figure 5.2-16) (ME-095). Alternative dryers are multiple hearth incinerators and rotary kilns. The dewatered sludge has a moisture content of less than 10 percent (ME-095). Pretreatment of the sludge by filtration or centrifugation may be desired to lower the heat requirement for drying the sludge. Spray drying may also be used for drying of sludge but application has been extremely limited. A spray drying system is shown in Figure 5.2-17 (ME-095). Heat drying processes generally have high capital and operating costs.

5.2.5.7 LNG and SNG Plant Wastewater Treating

The LNG and SNG plants have very small wastewater streams. In the LNG plant boiler blowdown is recycled through demineralizers and thus the only major process wastewater source is regenerant wastes from the blowdown. The major constituent of the effluent stream is dissolved salts. Water effluents from the process area will be slightly oily due mostly from lubricants. A dike system around the processing area will contain oily process effluent water. The oily wastewater is processed by a oily water separator of the CPI (corrugated plate inteceptor) type. The separator effluent can be treated with a small coagulation, sedimentation, or filtration system. The final effluent can be wasted to an evaporation pond if there is enough land area. To protect the environment against potentially polluting fluids the evaporation pond should be constructed of concrete or asphalt or lined with a flexible membrane liner. If land is not available the effluent can be drained directly into the municipal sewer system. A holding tank of some sort should be included to contain possible spills in the processing area.

FIGURE 5.2-16

FLASH-DRYING SYSTEM WITH MIXED REFUSE INCINERATOR [FROM COMBUSTION ENGINEERING]

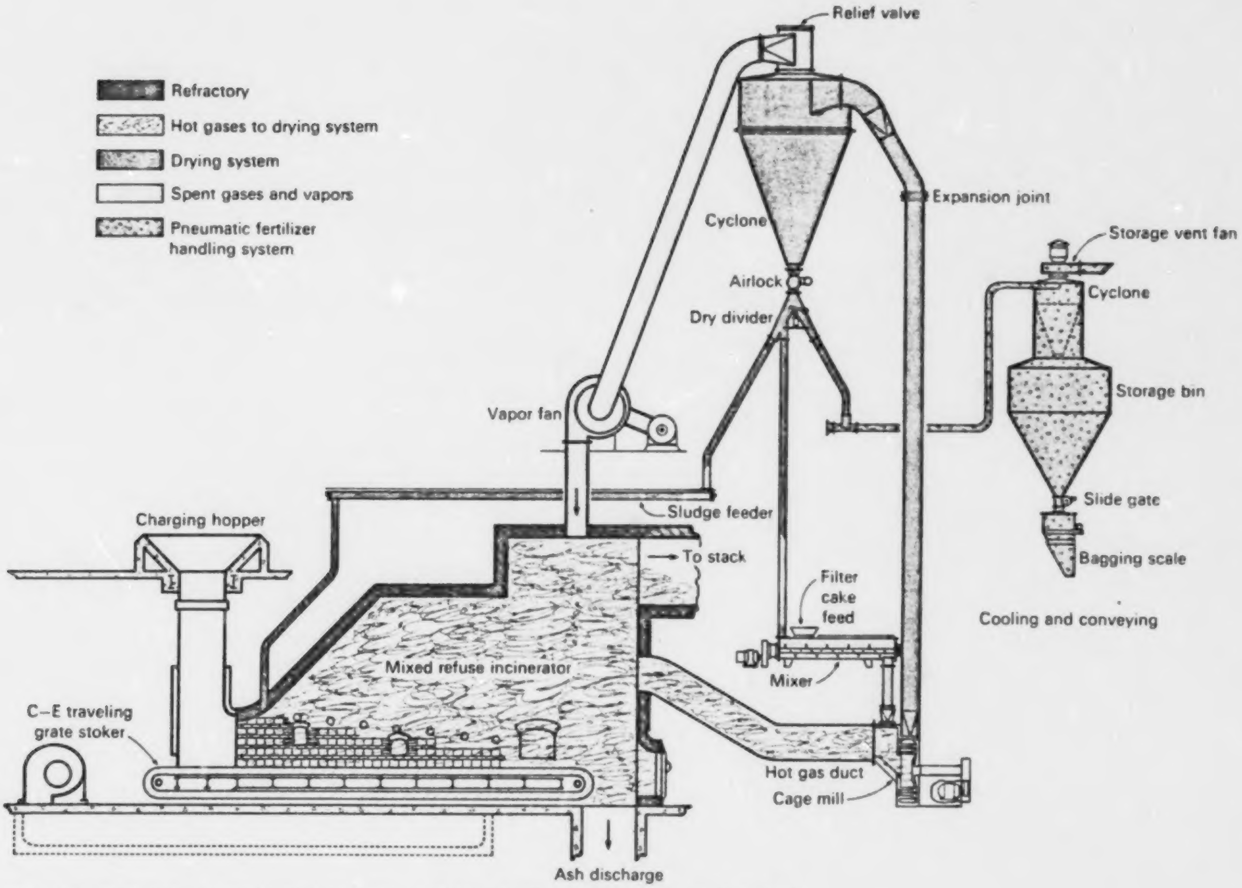
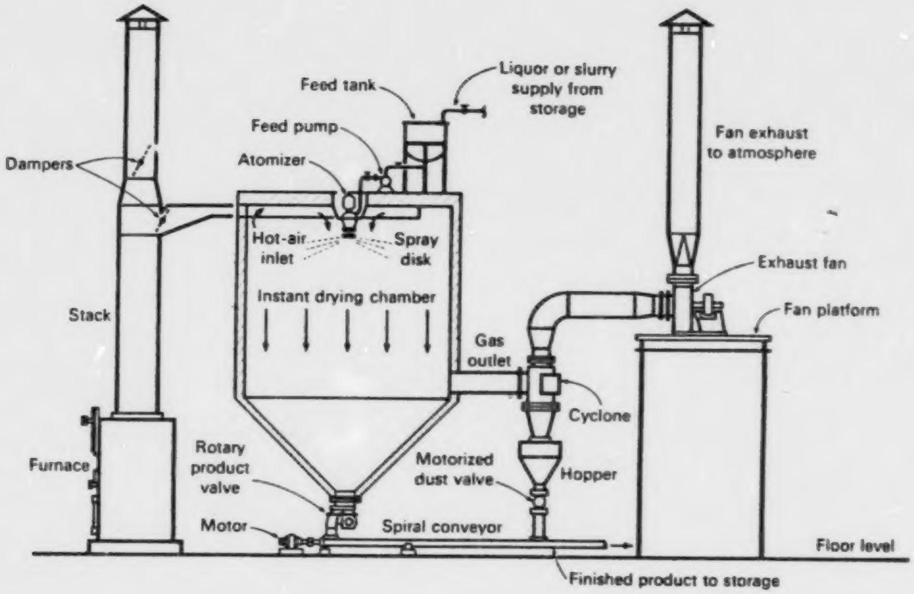

Refractory
Hot gases to drying system
Drying system
Spent gases and vapors
Pneumatic fertilizer handling system
Relief valve
Expansion joint
Cyclone
Storage vent fan
Cyclone
Airlock
Dry divider
Storage bin
Vapor fan
Slide gate
Sludge feeder
Charging hopper
To stack
Bagging scale
Filter cake feed
Cooling and conveying
Mixed refuse incinerator
Mixer
C–E traveling grate stoker
Hot gas duct
Cage mill
Ash discharge

FIG. 8-20 Flash-drying system with mixed refuse incinerator [from Combustion Engineering].

FIGURE 5.2-17

SPRAY DRYER WITH PARALLEL FLOW
[FROM INSTANT DRYING COMPANY]


Feed tank
Liquor or slurry supply from storage
Feed pump
Atomizer
Dampers
Fan exhaust to atmosphere
Hot-air inlet
Spray disk
Exhaust fan
Instant drying chamber
Stack
Fan platform
Gas outlet
Cyclone
Furnace
Rotary product valve
Motorized dust valve
Hopper
Motor
Spiral conveyor
Floor level
Finished product to storage

The SNG plant will have a greater wastewater effluent rate per Btu fuel produced than the LNG plant. The increased effluent flow is mainly due to a large steam load and waste solution from the Benfield system. The same treatment facilities used in the LNG plant can be used in the SNG plant.

Other techniques for reducing the wastewater effluent rate for LNG or SNG plants include use of air cooling, design of a system using a minimal amount of energy, recycle of water wherever possible, and use of proper cleaning and housekeeping methods.

5.2.6 Summary

The wastewater treatment units and procedures described in this section have been or potentially can be applied to the wastewater from refineries, SNG plants, and LNG plants. It should be noted that the information given for processes for which no refinery, SNG plant or LNG plant application has been cited is from municipal wastewater treatment facilities. Consideration must therefore be given to the differences in industrial wastewater and municipal wastewater in order to apply these processes.

Sludge combustion and sludge and ash disposal are discussed in the following section on Solids Emission Control.

5.3 Solids Emission Control

The LNG plant has no appreciable solid wastes associated with the production site. The SNG plants have solid spent catalyst wastes which are generated on an intermittent basis. The amount of catalyst is small and is suitable for landfill and thus poses no real pollution problem. Solid wastes from a refinery consist of dirt, grit, oily sludges, and settled out sludges removed in the primary treatment processes, bacterial sludges removed in the secondary treatment clarifiers, chemical sludges resulting from chemical treatment of the wastewater, and finally, intermittent spent catalysts.

5.3.1 Sludge Disposal Methods

The dirt and grit obtained from the grit chamber are disposed of in landfills. The oily sludges, primary clarifier sludges, bacterial sludges, and chemical sludges which have been dewatered or dried can be handled in various methods.

The most popular methods for sludge disposal in the past have been ocean dumping or drying in open beds followed by landfill (SO-080). Problems have arisen with both methods which make them unfeasible for disposal methods. The ocean dumping method is being strictly regulated and eliminated where possible by Federal and local government. Drying in open beds or evaporation ponds can create major odor problem. Another problem is that open beds also require a large land area which may not be available to modern refineries located in metropolitan areas. Suitable landfill areas required for the dried sludge may also become scarce within populated areas and thus present a problem of transportation of the sludge to the proper landfill site.

Chemfix Process

A recently developed landfill method for handling of sludge waste is the Chemfix process (WI-144). In this process, a three phase reaction forms a chemical matrix which traps the sludge in a pseudomineral material which is suitable for landfill. Advantages of the process are relatively low cost, controlled rate of solidification, high continous throughput rate, mobility, small volume increase due to chemical additives, ability to react with complex waste mixtures, ability to process low-solids wastes without discharge from the process, and nontoxicity of the solid material (WI-144).

Incineration

One alternative to landfill is sludge incineration. The type of incinerator used is dependent on the moisture content of the sludge. Rotary kilns can operate over a wide range of 5 to 70 percent solids. Lower solid concentrations, 2 to 10 percent, will require a special fluidized sand bed incinerator, while higher concentrations, 40 to 70 percent can be combusted in a simpler stationary multiple hearth incinerator (RA-081). In order to obtain these concentrations some type of thickener must be employed. Thickeners are discussed in the wastewater treatment section of this report (Section 5.2).

The economics of sludge incineration show that for small lean sludge quantities concentration is not economically feasible, while large lean streams prove economical to concentrate in order to reduce the size of the incinerator required (RA-081).

American Oil Company's Mandan, North Dakota, refinery presently uses a fluidized hot sand incinerator (MA-226). The incinerator has the added advantage of being able to incinerate spent caustic from various refinery units. The solids from the incinerator can be landfilled or used as an excellent substitute for a mixture of sand and rock salt used on icy roads (MA-226). The Mandan incinerator is shown in Figure 5.3-1.

Sludge Spraying on Land

Another sludge disposal method is spraying dilute sludge on poor soils to increase fertility (SO-080). Sludge injection into the soil has also been suggested to help eliminate odor problems involved with spraying. Methods such as these, however, require a market for the sludge and a means of transporting the sludge to the market.

Lagooning

Lagooning may be used as a simple and economical method for handling ultimate sludge disposal if the refinery is located in a remote area. In lagooning the sludge organic solids are stabilized by aerobic and anaerobic decompostion which may give rise to objectionable odors (ME-095). To avoid material buildup the stabilized sludge will have to be removed from the basins intermittently.

Fertilizer Production

Sludge may be also handled by heat drying and treating to produce a fertilizer. Technology for fertilizer production exists, but the major problem arises from finding a market for selling the fertilizer. Heat treatment costs and transportation costs also raise the price of the final fertilizer product.

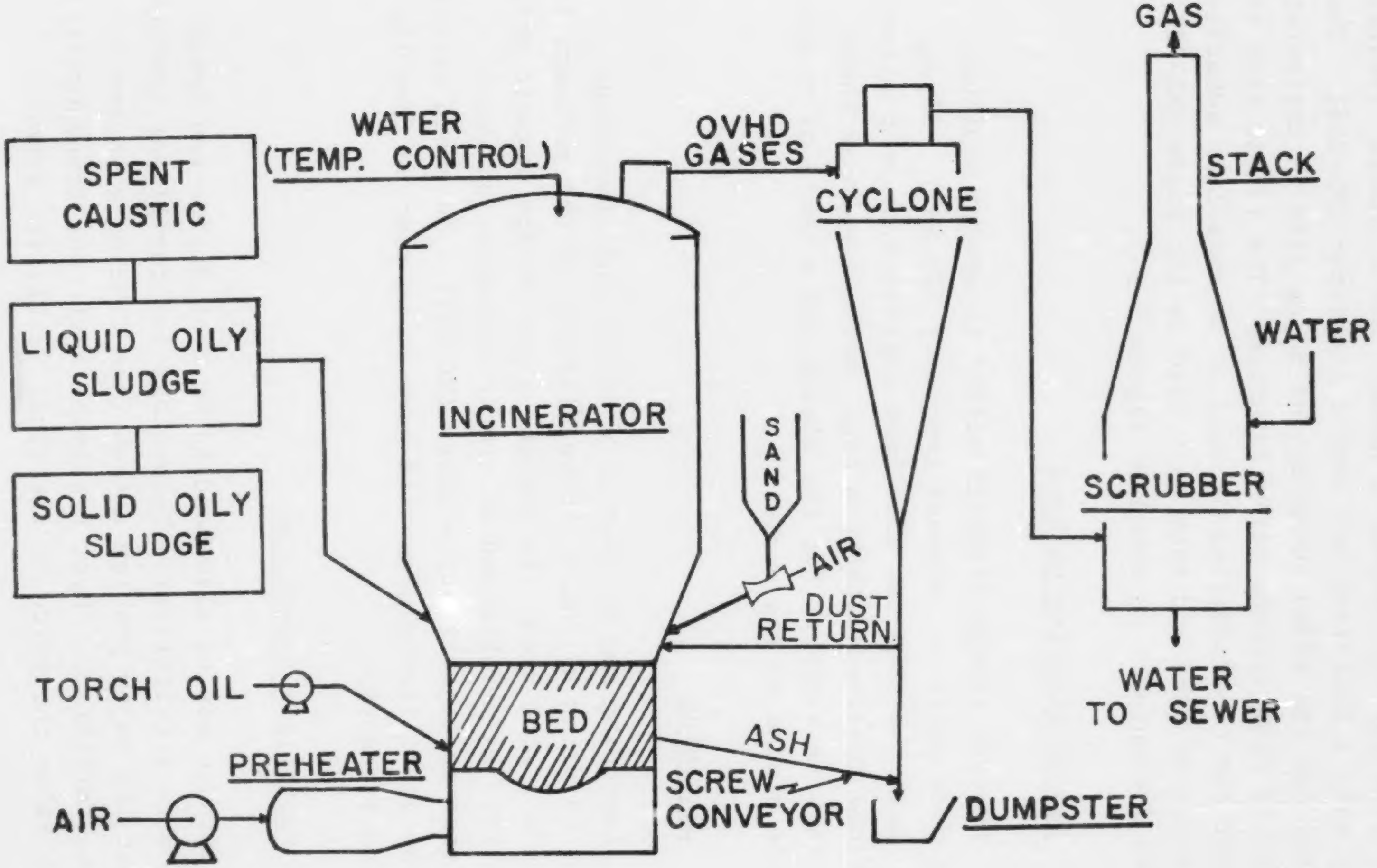

WATER
(TEMP. CONTROL)
OVHD
GASES
GAS
SPENT
CAUSTIC
CYCLONE
STACK
LIQUID OILY
SLUDGE
WATER
INCINERATOR
SAND
SCRUBBER
SOLID OILY
SLUDGE
AIR
DUST
RETURN
WATER
TO SEWER
TORCH OIL
BED
ASH
PREHEATER
SCREW
CONVEYOR
AIR
DUMPSTER

FIGURE 5.3-1 FLUIDIZED BED INCINERATOR
Source: AM-020

WET OXIDATION

Wet oxidation is a process for destruction of dissolved or suspended organic matter by oxidizing with air at temperatures above the normal boiling point of water (212°F, 100°C), and under pressure. The process has been used traditionally to treat sewage sludge but is finding new applications in industrial wastewater treatment. Zimpro Inc., Rothschild, WI, has over 130 units in operation or under construction, several operating on coke oven gas liquors and ethylene cracking wastewater.

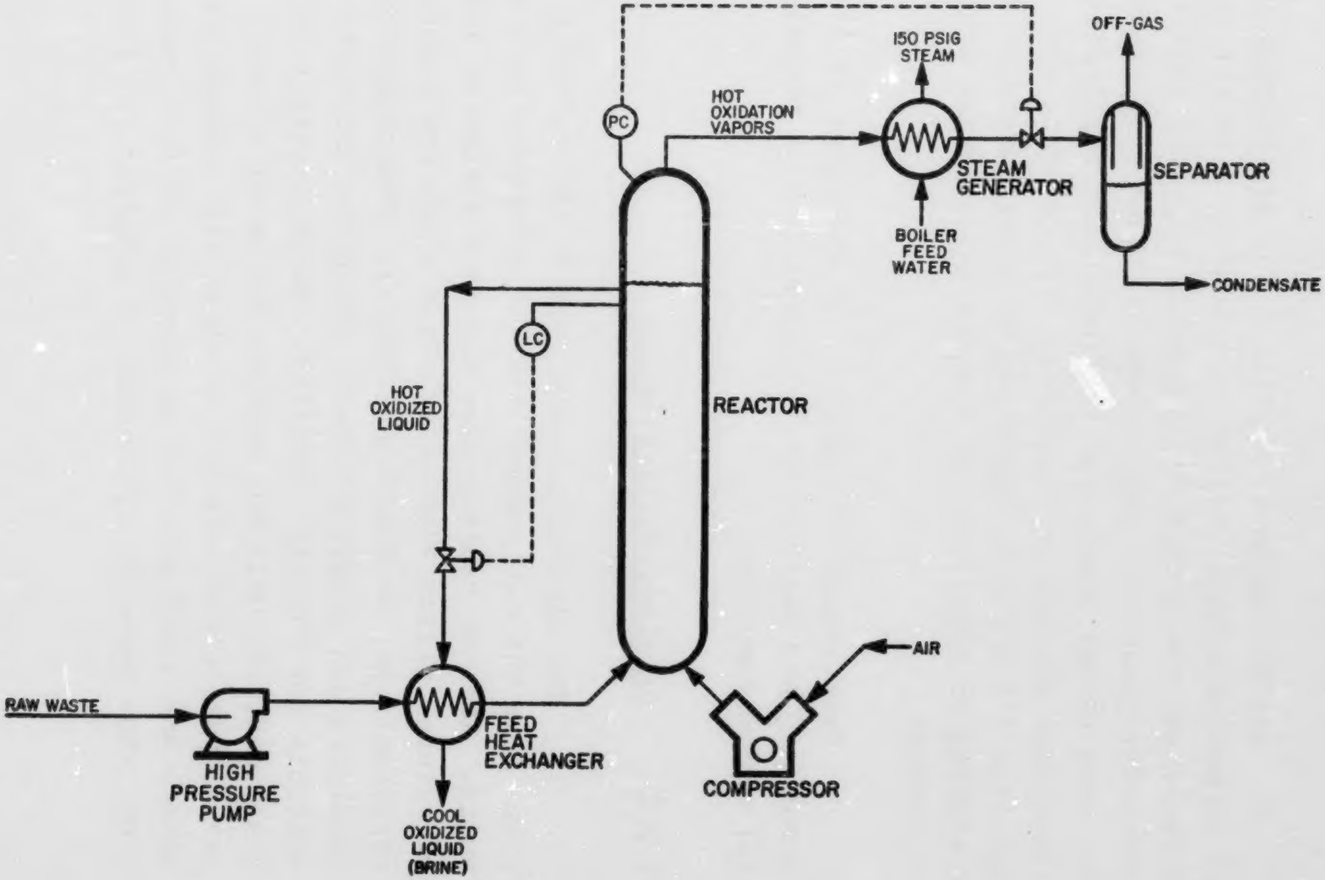
Performance is typically in the range of 90-95% COD reduction, and better than 99% reductions in phenolics, cyanide, and sulfur compounds.

5.3.2 Catalyst Solid Disposal

The disposable catalysts in the refinery are those from the cat cracker and the hydrodesulfurization units. The cat cracker uses either a synthetic silica alumina or natural silica alumina catalyst which are highly inert and applicable to landfilling (NE-044). Hydrodesulfurization catalysts are generally inert, non-noble catalysts which are suitable for landfill (RA-119). Noble catalyst will not be discarded, but will be recycled for metal values. The spent resid hydrodesulfurization catalyst will contain vanadium and nickel and could possibly be disposed of to a recovery operation, thus reducing the amount of catalyst requiring disposal.

FIGURE 5.3-2

GENERALIZED FLOW SCHEME FOR A ZIMPRO® WET AIR OXIDATION UNIT


OFF-GAS
150 PSIG STEAM
HOT OXIDATION VAPORS
PC
STEAM GENERATOR
SEPARATOR
BOILER FEED WATER
CONDENSATE
LC
HOT OXIDIZED LIQUID
REACTOR
AIR
RAW WASTE
FEED HEAT EXCHANGER
HIGH PRESSURE PUMP
COMPRESSOR
COOL OXIDIZED LIQUID (BRINE)

(From Zimpro, Inc.)

6.0 PLANT IMPACT AND SITING PROBLEMS

The purpose of this section is to identify the environmental impact and siting problems of new refineries, SNG and LNG plants, and their associated support facilities. To accomplish these tasks, basic information on the type, size, and the specific location of the plant or refinery is required. Appropriate premises have been set for purposes of this report. Modules of the following type and size are considered:

- Refinery
  - Oil: 200,000 bbl/day
  - Gasoline: 200,000 bbl/day

- SNG Plant: 125 MM scf/day of SNG produced

- LNG Plant
  - Peak Shaving: 100 MM scf/day
  - Base Load: 750 MM scf/day

The environmental consequences investigated are primarily the gaseous effluents to the ambient air, the wastewater effluents to the receiving waters, and the solid wastes for disposal. The effects of these effluents on the air and water quality in the area where an oil refinery, an SNG plant, or an LNG plant is intended to be located can be best described through use of available computational schemes, such as ambient air and water impact models. The results of these computations can be compared with the existing local, state, and Federal regulations.

This study does not call for a specific site; however, impacts are site specific. For this report, a comparative analysis is used. The approach is to compare the effluents of the modules in this study with the effluents from a reference module on which extensive environmental impact investigations have been performed. To achieve a meaningful comparison, it is assumed that the stack parameters, meteorological conditions, receiving water body conditions, and process control technology for the reference modules and for those presented in this report are the same.

Siting problems related to feedstock availability and its transportation, energy, water requirements (circulating and makeup water), product transportation, and status of Federal, state, and local laws are identified and discussed in general terms.

The environmental impact and siting problems of the modules are studied in a conservative manner. This implies that the major support facilities (power plant, storage farm, and marine terminal) are integral parts of the oil refinery, SNG, and LNG plant sites. The environmental consequences and siting problems of the modules are presented and discussed in the following pages.

6.1 Petroleum Refinery Impact

This study considers fuel oil and gasoline refineries. Each of the two refinery types is characterized as a module with a feed capacity of 200,000 bbl/calendar day (bpcd) of raw crude. Detailed descriptions of the fuel oil and gasoline refinery modules are presented in Sections 3.1 and 3.2.

This section deals with refinery effluents and regulations, raw material availability, water requirements, and product transportation.

6.1.1 Refinery Effluents

Refinery effluents of primary concern in this report are air emissions, water effluents, and solid wastes. Their impact can be assessed by estimating the impacts of each on ambient air and water quality.

6.1.1.1 Air Emissions Impact

Reasonable estimates of the impact on ambient air quality which might result from the location of a new petroleum refinery at a given site can be obtained by using air dispersion models. There are three types of models; short-term average, long-term average, and 24-hour (hybrid). The models are based on the Gaussian dispersion approximation originally formulated by Sutton (SU-044) and modified by Pasquill (PA-095) and by Gifford (GI-035).

The long-term average model uses historial meteorological data to estimate annual average pollutant concentrations. These estimated annual averages and certain statistical assumptions (LA-100) are then used to estimate maximum concentrations for averaging times less than one year. The short-term model computes estimated concentrations corresponding to a 10-minute averaging time. A statistical assumption (TU-020), different from that employed in the annual average model, is used to transform the 10-minute average estimates to estimates corresponding to other averaging times. The 24-hour model is, in essence, a hybrid of the two models, in that it incorporates some of the averaging features of the long-term model with the statistical assumptions of the short term model.

The atmospheric dispersion models require specific information for input data. This information consists of estmated emissions, the refinery configuration, and meteorological data. The computed air emissions of the 200,000 bpcd refinery modules, given in Sections 3.1 and 3.2, are summarized in Table 6.1-1. In addition, Table 6.1-1 shows a summary of the calculated air emissions of a reference refinery model based on a gasoline refinery with a feed capacity of 300,000 bpcd of raw crude (RA-181).

In Table 6.1-1, the particulates released by the 200,000 bpcd gasoline refinery module are 440 lb/hr compared to 353 lb/hr from the 300,000 bpcd reference module. Some of the units in the gasoline refinery module, such as crude distillation, heavy naphtha reformer, heavy hydrocrackate reformer and hydrogen plant are fuel oil fired units; thus, they produce higher particulate emissions than the predominantly gas fired units in the reference modules as indicated in Table 6.1-2.

Refinery Configuration

The basic process elements of a refinery complex which give rise to gaseous pollutant emissions include distillation, hydro-desulfurization, catalytic cracking, reforming, and isomerization. Power plant combustion processes also contribute to pollutant emissions. Finally, fugitive losses of hydrocarbons from process and storage areas must also be considered as emission sources.

Besides the pollutant emissions from the major sources, ambient air quality in the plant vicinity depends on the spatial distribution and physical characteristics of the emission sources. Consequently, to make definite predictions concerning pollutant dispersion, it is necessary to specify the locations and physical stack heights for each of the major sources in the refinery complex.

TABLE 6.1-1

REFINERY AIR EMISSIONS

Pollutant	200,000 BPCD Fuel Oil Refinery Module	200,000 BPCD Gasoline Refinery Module	300,000 BPCD Gasoline Refinery (Reference)
Particulates, lb/hr.	263	432[1]	353
Sulfur Dioxide (SO_2), lb/hr.	667	948	1,918[2]
Hydrocarbons (HC), lb/hr.	3,082	3,200	6,418[3]
Carbon Monoxide (CO), lb/hr.	50	95	138[4]
Nitrogen Oxides (NO_x), lb/hr.	493	1,250	1,846[4]

---

[1] Excessive particulate emissions are due to the combustion of some fuel oil in the gasoline refinery module whereas only fuel gas is combusted in the reference refinery.

[2] The larger SO_2 emission rate is due to a larger volume of tail gas being emitted from the reference refinery which is a result of a higher percentage of sulfur in the crude.

[3] The larger hydrocarbon rate is due to the greater crude and petroleum storage capacity in the reference refinery.

[4] These values are comparable on a size of refinery basis.

TABLE 6.1-2

EMISSIONS AND STACK PARAMETERS 300,000 BPCD GASOLINE REFINERY (REFERENCE MODULE) [1]

Source	Heat [2] Input MM Btu/Hr	Process Gas Fired	Emissions lbs/hr [3]					Stack Parameters [4]					
			Particulates	SO_2	Total Organics	CO	NO_x	Mass Flow lbs/hr	ACFM	Velocity fps	Height ft.	Temp. °F	Diameter ft.
1) No. 1 Crude Unit ATM. Dist. Htr.	500	$765\mathrm{x}10^3$	8.6	20.5	1.43	8.1	110	$510\mathrm{x}10^3$	$196\mathrm{x}10^3$	60	200	450	8.33
2) No. 1 Crude Unit Vac. Dist. Htr.	125	$191\mathrm{x}10^3$	2.15	5.14	0.358	2.03	27.4	$128\mathrm{x}10^3$	$49\mathrm{x}10^3$	60	200	450	4.16
3) No. 2 Crude Unit ATM. Dist. Htr.	500	$765\mathrm{x}10^3$	8.60	20.5	1.43	3.1	110	$510\mathrm{x}10^3$	$196\mathrm{x}10^3$	60	200	450	8.33
4) No. 2 Crude Unit Vac. Dist. Htr.	125	$191\mathrm{x}10^3$	2.15	5.14	0.358	2.03	27.4	$128\mathrm{x}10^3$	$49\mathrm{x}10^3$	60	200	450	4.16
5) No. 1 De-asphalting Unit	317	$484\mathrm{x}10^3$	5.40	13.0	0.905	5.10	69.5	$324\mathrm{x}10^3$	$124\mathrm{x}10^3$	60	200	450	6.62
6) No. 2 De-asphalting Unit	317	$484\mathrm{x}10^3$	5.40	13.0	0.905	5.10	69.5	$324\mathrm{x}10^3$	$124\mathrm{x}10^3$	60	200	450	6.62
7) Gas Oil NDS Unit	117	$178\mathrm{x}10^3$	1.99	4.78	0.332	1.88	25.5	$119\mathrm{x}10^3$	$45.7\mathrm{x}10^3$	60	200	450	4.02
8) Resid HDS Unit	108	$165\mathrm{x}10^3$	1.86	4.43	0.310	1.76	23.7	$111\mathrm{x}10^3$	$42.4\mathrm{x}10^3$	60	200	450	3.87
9) S.R. Naphtha HDS Unit	70.8	$108\mathrm{x}10^3$	1.22	2.90	0.202	1.15	15.6	$72.5\mathrm{x}10^3$	$27.8\mathrm{x}10^3$	60	200	450	3.14
10) S.R. Naphtha Reforming Unit	588	$896\mathrm{x}10^3$	10.1	24.1	1.67	9.50	128	$599\mathrm{x}10^3$	$230\mathrm{x}10^3$	60	200	450	9.02
11) Isomerization Unit	20.8	$31.8\mathrm{x}10^3$	0.357	0.85	0.0595	0.337	4.56	$21.2\mathrm{x}10^3$	$8.2\mathrm{x}10^3$	60	200	450	1.70
12) Hydrocracking Unit	425	$650\mathrm{x}10^3$	7.31	17.4	1.22	6.90	93.3	$435\mathrm{x}10^3$	$167\mathrm{x}10^3$	60	200	450	7.68
13) H.C. Naphtha HDS Unit	41.7	$63.8\mathrm{x}10^3$	0.716	1.71	0.119	0.676	9.17	$42.7\mathrm{x}10^3$	$16.4\mathrm{x}10^3$	60	200	450	2.41
14) H.C. Naphtha Reforming Unit	442	$675\mathrm{x}10^3$	7.57	18.1	1.27	7.16	96.7	452.10^3	$173\mathrm{x}10^3$	60	200	450	7.83
15) Alkylation Unit	108	$165\mathrm{x}10^3$	1.86	4.43	0.310	1.76	23.7	$111\mathrm{x}10^3$	$42.4\mathrm{x}10^3$	60	200	450	3.87

TABLE 6.1-2
EMISSIONS AND STACK PARAMETERS 300,000 BPCD GASOLINE REFINERY (REFERENCE MODULE)
Page Two

			Emissions lbs/hr [3]					Stack Parameters [4]					
Source	Heat Input MM Btu/Hr	Fuel SCFM	Particulates	SO_2	Total Organics	CO	NO_x	Mass Flow lbs/hr	ACFM	Velocity fps	Height ft.	Temp °F	Diameter ft.
16) Mid.Dist. HDS Unit	138	210×10^3	2.36	5.64	0.392	2.22	30.1	141×10^3	54×10^3	60	200	450	4.37
17) FCCU Unit	333	508×10^3	5.72	13.6	0.95	5.40	73.0	340×10^3	131×10^3	60	200	450	680
18) FCCU Regenerator [5]			34.4	395	15.4	13.8	359	724×10^3	243×10^3	60	200	350	9.27
19) Partial Oxidation No. 1 [6]	10.9	16.6×10^3	0.186	0.44	0.031	0.176	2.38	11.1×10^3	4.2×10^3	60	200	450	1.22
20) Partial Oxidation Nos. 2 and 3 [6]	21.7	33.2×10^3	0.372	0.89	0.062	0.352	4.76	22.1×10^3	8.48×10^3	60	200	450	1.73
21) Partial Oxidation Nos. 4 and 5 [6]	54.9	84.2×10^3	0.942	2.26	0.157	0.892	12.1	56.1×10^3	21.5×10^3	60	200	450	2.76
22) A-Steam Generation	1108	[7]	137	629	22.2	26.3	281	1060×10^3	404×10^3	60	200	450	11.76
22) B-Electrical Generation	933	[7]	98	531	18.7	22.2	238	890×10^3	342×10^3	60	200	450	11.0
23) Sulfur Recovery [8]				150				1950×10^3	727×10^3	60	200	450	16.04
24) Sludge Incineration			8.40	34.4	1.35	5.49	12.0	40×10^3	15.3×10^3	60	200	450	2.33
25) Miscellaneous [9]					3810						17		
26) Petroleum Storage			——	——	2538	——	——				50		
Total			353	1918	6418	138	1846						

---

[1] One emission source per process or processing square (plot plan) was used with the following exceptions:

A. ATM and Vac. Htrs. - No. 1 Crude Unit
B. ATM and Vac. Htrs. - No. 2 Crude Unit
C. S.R. Naphtha HDS and Reforming Units
D. H.C. Naphtha HDS and Reforming Units

[2] Unit heat requirements determined from (RA-119) and MY-013).

[3] Stack emissions determined from EPA emission factors for natural gas and fuel oil (EN-071).

[4] Assumptions used for stack parameters:

Velocity - 60 FPS
Temperature - 450°F
Height - 200 ft. (initial estimate)

[5] FCCU Regenerator Ohd. gas calculated from (HA-157).

[6] Partial oxidation emissions and rates were split

[7] Heat required from fuel oil (22.5% of total heat requirements) is assumed to be utilized for power generation.

[8] Sulfur recovery facilities assumed to be capable of 99.9% recovery (RA-119). Sulfur recovery tail gas rates estimated from (BE-148).

[9] Miscellaneous HC emissions were assumed to be 0.1 wt% of charge (EN-043).

SOURCE: (RA-181)

Stack parameters associated with process heaters are selected on the basis of current trends in the refining industry. Heater flue gas outlet temperatures were set at 450°F, a relatively low temperature. This is because future high costs for fuels will make maximum heat recovery profitable. The stack heights were set at 200 feet, somewhat taller than current practice, in order to demonstrate maximum dispersion effects. Typical stack exit velocities were set at 60 ft/sec. Emissions from petroleum storage tanks are assumed to have a stack height of 50 feet, while fugitive losses in the processing area have a stack height of 17 feet.

The physical configuration of the sources within the site area for the 300,000 bpcd reference module is shown in Figure 6.1-1. The two refinery modules are assumed to be built in approximately the same configuration and in such a way that geometrical symmetry is preserved. The orientation of the site is such that the line of the stacks is at right angles to the prevailing wind.

Meteorological Data

Two sets of meteorological data are necessary for estimating the short-term and annual average maximum concentrations. These data consist of 24-hour and annual meteorological conditions. The 24-hour data are specifically employed when computing short-term maximum concentrations. The annual meterological information is used when calculating annual average maximum concentrations.

Climatological conditions vary from one area to another. An arbitrary representative site was chosen as a basis for selecting meteorological data. In estimating maximum concentrations at the selected location, questions of the following nature were considered:

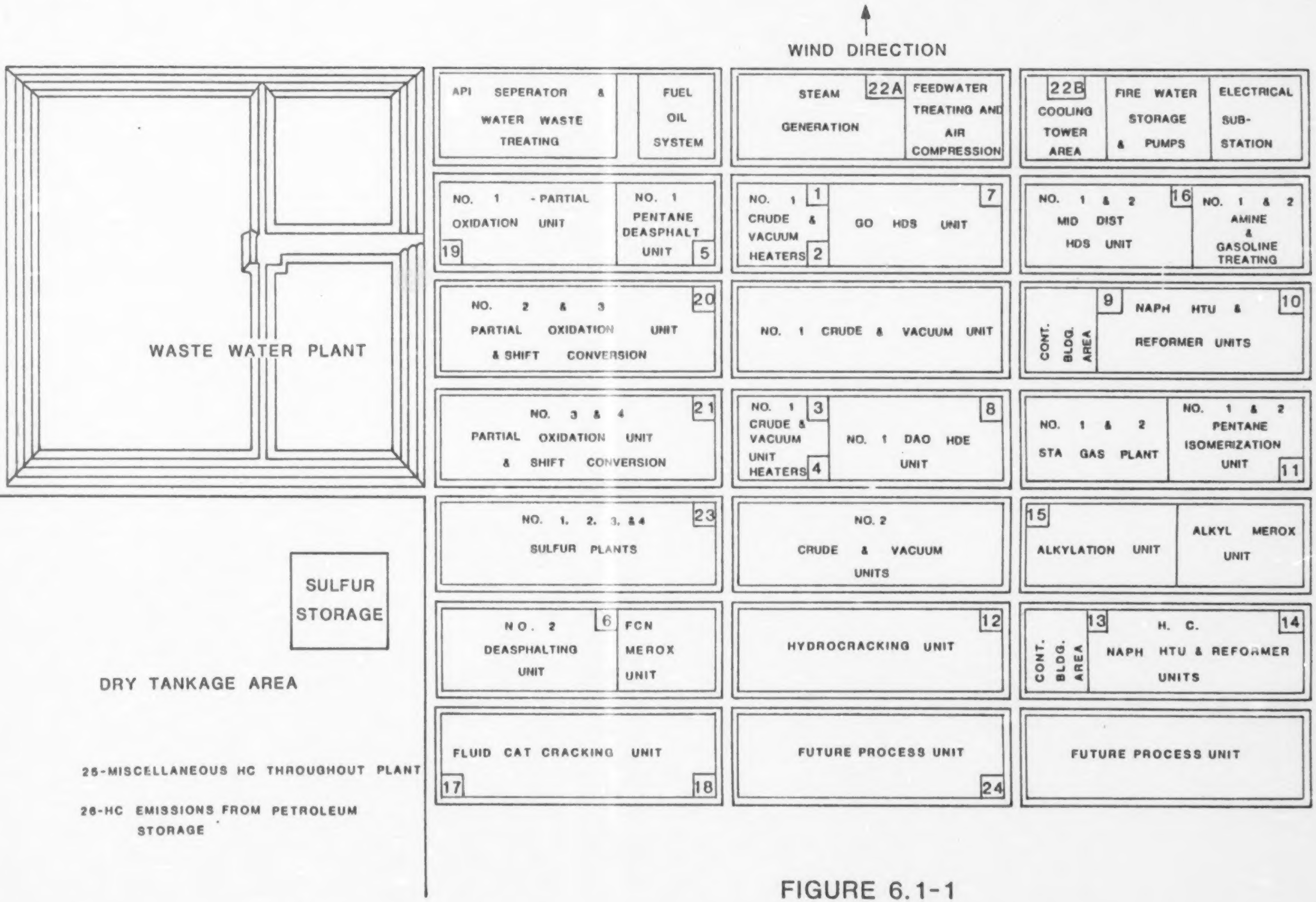

WIND DIRECTION
WASTE WATER PLANT
SULFUR STORAGE
DRY TANKAGE AREA
25-MISCELLANEOUS HC THROUGHOUT PLANT
26-HC EMISSIONS FROM PETROLEUM STORAGE
API SEPERATOR & WATER WASTE TREATING
FUEL OIL SYSTEM
STEAM GENERATION
22A
FEEDWATER TREATING AND AIR COMPRESSION
22B
COOLING TOWER AREA
FIRE WATER STORAGE & PUMPS
ELECTRICAL SUB-STATION
NO. 1 - PARTIAL OXIDATION UNIT
19
NO. 1 PENTANE DEASPHALT UNIT
5
NO. 1 CRUDE & VACUUM HEATERS
1
2
GO HDS UNIT
7
NO. 1 & 2 MID DIST HDS UNIT
16
NO. 1 & 2 AMINE & GASOLINE TREATING
NO. 2 & 3 PARTIAL OXIDATION UNIT & SHIFT CONVERSION
20
NO. 1 CRUDE & VACUUM UNIT
CONT. BLDG. AREA
9
NAPH HTU & REFORMER UNITS
10
NO. 3 & 4 PARTIAL OXIDATION UNIT & SHIFT CONVERSION
21
NO. 1 CRUDE & VACUUM UNIT HEATERS
3
4
NO. 1 DAO HDE UNIT
8
NO. 1 & 2 STA GAS PLANT
NO. 1 & 2 PENTANE ISOMERIZATION UNIT
11
NO. 1, 2, 3, & 4 SULFUR PLANTS
23
NO. 2 CRUDE & VACUUM UNITS
15
ALKYLATION UNIT
ALKYL MEROX UNIT
NO. 2 DEASPHALTING UNIT
6
FCN MEROX UNIT
HYDROCRACKING UNIT
12
CONT. BLDG. AREA
13
H. C. NAPH HTU & REFORMER UNITS
14
FLUID CAT CRACKING UNIT
17
18
FUTURE PROCESS UNIT
24
FUTURE PROCESS UNIT

FIGURE 6.1-1

HYPOTHETICAL CONFIGURATION OF A 300,000 BPCD GASOLINE REFINERY (REFERENCE MODULE)

- What is the probability that a "worst" case for 24-hour data from a selected area can occur at any location at least once within a year?

- Is there a general behavior pattern for pollutant dispersions on an annual basis?

The first question considers whether a set of 24-hour meteorological data from a given area at a certain time of the year (for example that of Brazoria, Texas, given in Table 6.1-3), that is considered "worst" from the standpoint of maximum concentrations, can also occur elsewhere at other times of the year. The second question pertains to a situation where the annual pollutant dispersion can be characterized in general terms.

Concentrations of air pollutants are functions of dilution and diffusion processes. The absence of either process results an increase of ground level concentration. In the free atmosphere, both of these processes depend almost entirely on familiar meteorological parameters, viz, atmospheric stability, wind speed and direction, mixing depth, temperature, turbulence, precipitation, inversions, etc. These parameters, one way or another, are interrelated.

The first four parameters are the meteorological input conditions required by the atmospheric dispersion models; an example is the 24-hour climatological conditions for Brazoria, Texas in a typical July as shown in Table 6.1-3. This particular location, during a typical July, might exhibit six types of atmospheric stability classes. These are identified as types A, B, C, D, E and F. "D" stability, a neutral type, occur nine hours during the 24-hour example period. When "D" stability

TABLE 6.1-3
"WORST" CASE METEOROLOGICAL CONDITIONS ASSOCIATED WITH THE OCCURRENCE OF HIGH 24-HOUR AMBIENT CONCENTRATIONS: BRAZORIA, TEXAS

TIME	STABILITY	TEMP	MIXING DEPTH	WIND SPEED
0100	F	65°F	400 meters	3 knots
0200	F	65°F	400 meters	3 knots
0300	F	65°F	400 meters	3 knots
0400	F	65°F	400 meters	3 knots
0500	F	65°F	400 meters	3 knots
0600	F	65°F	400 meters	3 knots
0700	D (day)	70°F	500 meters	5 knots
0800	D (day)	70°F	500 meters	5 knots
0900	C	73°F	600 meters	7 knots
1000	B	74°F	900 meters	7 knots
1100	A	80°F	1200 meters	5 knots
1200	A	80°F	1200 meters	5 knots
1300	A	80°F	1200 meters	5 knots
1400	A	80°F	1200 meters	5 knots
1500	B	84°F	1500 meters	7 knots
1600	B	84°F	1500 meters	7 knots
1700	C	85°F	1500 meters	10 knots
1800	D (day)	80°F	1200 meters	15 knots
1900	D (night)	80°F	1000 meters	15 knots
2000	D (night)	80°F	1000 meters	15 knots
2100	D (night)	80°F	1000 meters	15 knots
2200	D (night)	80°F	1000 meters	15 knots
2300	D (night)	80°F	1000 meters	15 knots
2400	D (night)	80°F	1000 meters	15 knots

occurs, pollutants tend to travel farther from the source before reaching the ground. For convenience, descriptions of the stability classes based on EPA's Climatological Dispersion Model (CDM) are listed as follows.

Stability Class	
A	Extremely unstable
B	Moderately unstable
C	Slightly unstable
D (day)	Neutral (daytime)
D (night)	Neutral to slightly stable (nighttime)
E + F	Stable to extremely stable

There is a high probability that the stability classes in Table 6.1-3 can occur at other places in the U.S. at different times of the year.

The 24-hour mixing depth (or height), wind speed, and direction parameters are difficult to quantify in general terms; for example, during summer, mean morning mixing depth decreases from south to north, then from the central regions it decreases past the mountain regions and then increases to the west coast. It increases eastward and exhibits the highest value along the Gulf Coast, as shown in Figures 6.1-2 and 6.1-3. The wind speed decreases from south to north, then from the central regions the wind speed alternately increases and decreases either westward or eastward. In the afternoon, the mixing depth, wind speed, and direction parameters change from the above behavior to that of the isopleths in Figures 6.1-4 and 6.1-5.

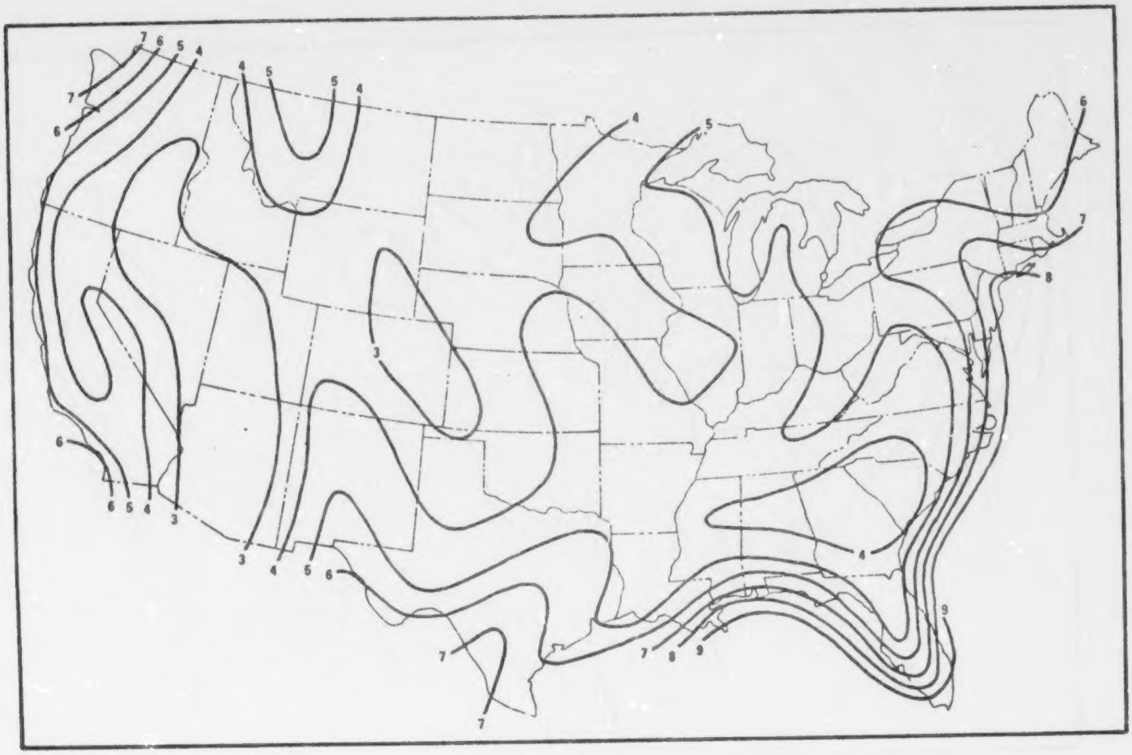

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FIGURE 6.1-2 ISOPLETHS (m x 10^2) OF MEAN ANNUAL MORNING MIXING HEIGHTS

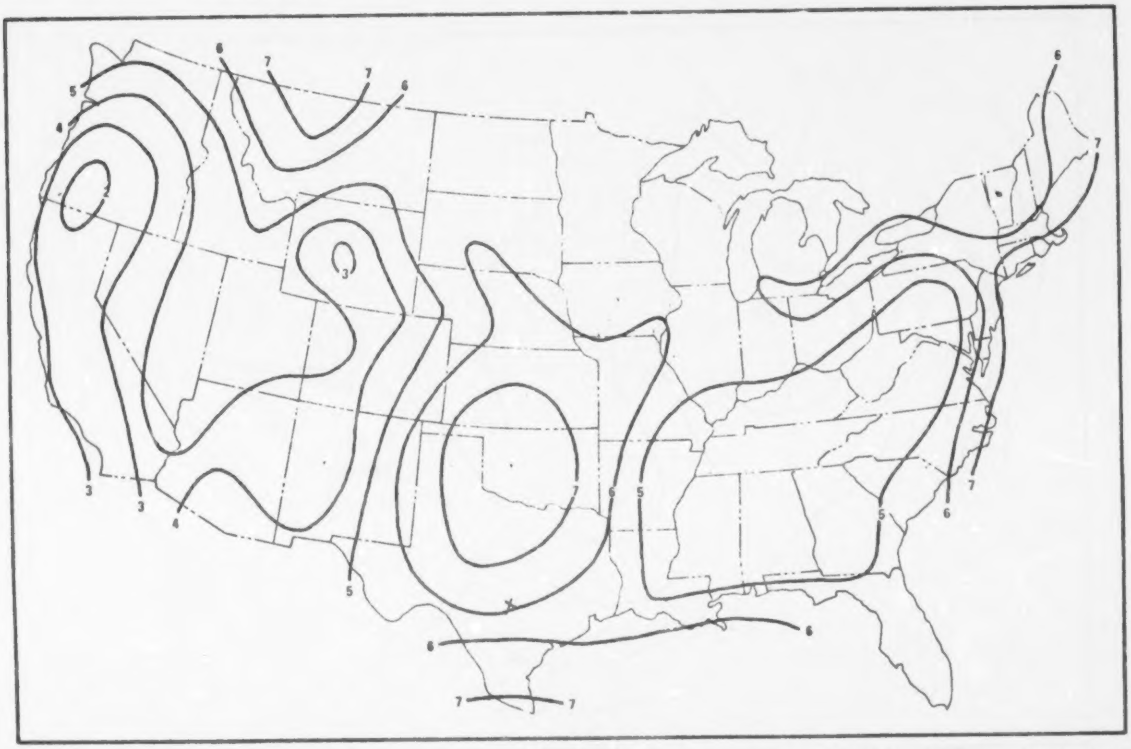
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FIGURE 6.1-3 ISOPLETHS (m sec^{-1}) OF MEAN ANNUAL WIND SPEED AVERAGED THROUGH THE MORNING MIXING LAYER

Source: (HO-049)

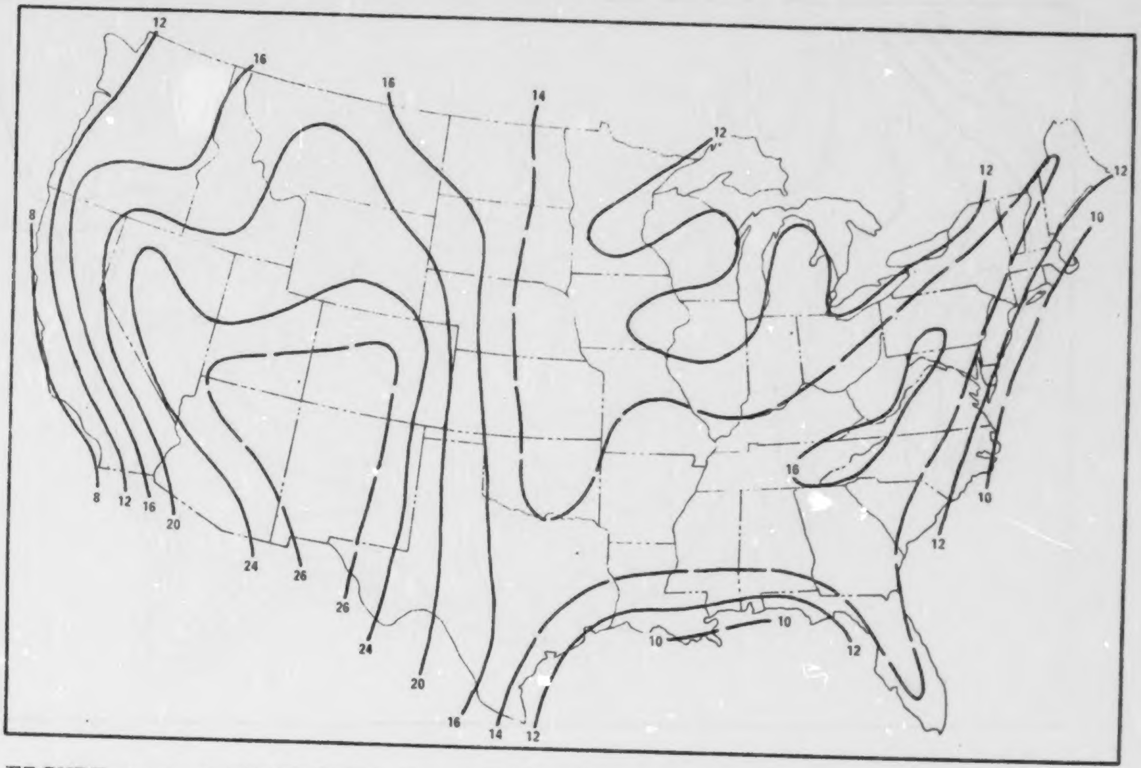
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FIGURE 6.1-4 ISOPLETHS (m x 10^2) OF MEAN ANNUAL AFTERNOON MIXING HEIGHTS

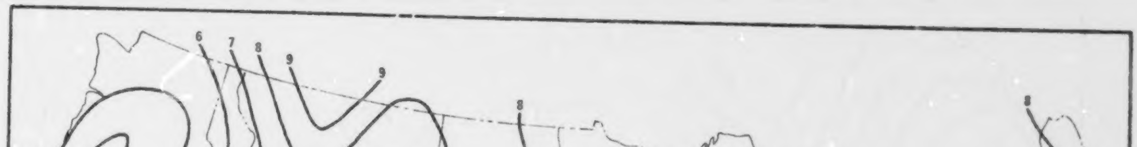
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FIGURE 6.1-5 ISOPLETHS (m sec^{-1}) OF MEAN ANNUAL WIND SPEED AVERAGED THROUGH THE AFTERNOON MIXING LAYER

Source: (HO-049)

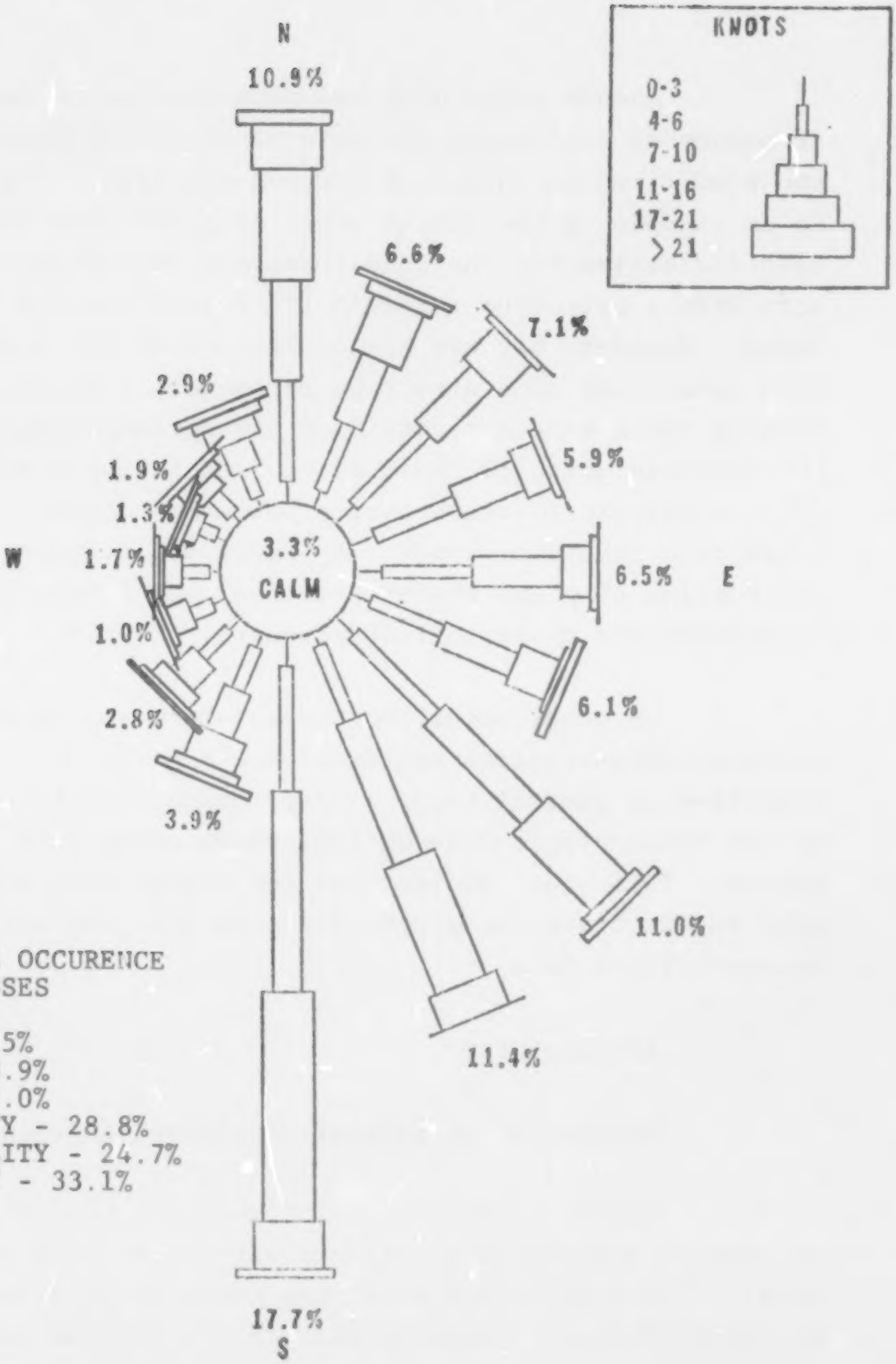
Annual meteorological data consist of the relative frequency of occurrence of the atmospheric stability classes and wind direction and speed during the year. Figure 6.1-6 is an example of the annual meteorological data that might be used for estimating the annual maximum concentrations of pollutants from a petroleum refinery if it were located in Brazoria, Texas. However, because the variations of the mixing height, wind speed, and wind direction parameters from the west coast towards the east coast, and from the northern regions towards the southern areas of the U.S., do not follow a definite pattern, it is difficult to characterize pollutant dispersion for all areas in a specific manner. Appendix 6.1-4 gives a general description of plume characteristics during various stability conditions and meterological parameter changes.

In other words, both short-term and annual average maximum concentrations estimated for a given site cannot be described in general terms simply because of the complex nature of the meteorological conditions which exist from region to region. This also implies that the atmospheric dispersion models must be exercised for a specific site with the appropriate meteorological data.

Example Cases

Dispersion of Refinery Pollutant Emissions

Recent studies have involved the use of dispersion models to predict maximum pollutant concentrations from petroleum refineries. These emissions were then compared to primary and secondary Federal standards and state and local ambient standards. Comparison to standards of other states, where instructive, were included, also. A description of the various atmospheric dispersion models used are given in Appendix 6.1-5.



ANNUAL PERCENTAGE OCCURENCE
OF STABILITY CLASSES

"A" STABILITY - .5%
"B" STABILITY - 3.9%
"C" STABILITY - 9.0%
"D(DAY)" STABILITY - 28.8%
"D(NIGHT)" STABILITY - 24.7%
"E & F" STABILITY - 33.1%

FIGURE 6.1-6 ANNUAL WIND ROSE -
VICTORIA, TEXAS 1964-1973

Basis for Examples

For the example case, it was assumed that the 300,000 bpcd reference refinery module described earlier in this report is sited in Brazoria, Texas. Meteorological conditions in Table 6.1-3 and Figure 6.1-6 along with the source emissions inventory shown in Table 6.1-2, were used as inputs to the previously described atmospheric dispersion models to compute the expected ground level pollutant concentrations.

Three schemes were considered in the analysis. For Scheme 1, the annual, short-term, and 24-hour maximum concentrations are computed using the data available for the 300,000 bpcd refinery module, and the results were compared with the existing ambient air quality standards. For Scheme 2, the annual, short-term and 24-hour maximum concentrations were computed in a manner similar to Scheme 1, but with the assumptions that the refinery module particulate emissions were increased by 50% and the resulting annual, short term, and 24-hour maximum concentrations were increased by 50%, 25%, and 25%, respectively. For Scheme 3, the annual, short-term, and 24-hour maximum concentrations were increased by 75%, 50% and 50% respectively. Schemes 2 and 3 were intended to represent gross estimates of maximum concentrations that can occur at any site in the U.S., and to indicate how these maximum concentrations compare with the existing ambient air quality standards. A summary of the bases for Schemes 1, 2, and 3 is given in Table 6.1-4. The following assumptions apply to the three schemes:

- A constant mean wind direction of 180° was assumed in making the 24-hour computations. This is a "worst" case consideration, meaning it will give rise to the highest maximum concentration for any set of meteorological conditions.

TABLE 6.1-4

SCHEMES USED IN EVALUATING EXPECTED GROUND LEVEL POLLUTANT CONCENTRATIONS

	Scheme 1	Scheme 2	Scheme 3
Particulate Emissions	No Increase	Increase by 50%	Increase by 50%
Annual Term Max. Conc.	No Increase	Increase by 50%	Increase by 75%
Short Term Max. Conc.	No Increase	Increase by 25%	Increase by 50%
24-Hour Term Max. Conc.	No Increase	Increase by 25%	Increase by 50%

- For shorter averaging times, two sets of conditions were used. The first corresponded to an unstable atmosphere, giving rise to maximum ground level concentrations due to emissions from tall stacks. (Stability Class A and a 5 knot wind speed were used for the unstable condition). The second set corresponded to a very stable atmosphere, and giving rise to maximum ground level concentrations due to emissions of non-buoyant material near the ground (fugitive hydrocarbon losses). Stability class E and a 2 knot wind speed are used for the stable condition.

- The probability of the unstable condition occurring is low. The second set of conditions, however, represented a typical nighttime condition. For comparison purposes, a more typical daytime condition (represented by stability class D and a wind speed of 9 knots) was also considered.

Tables 6.1-5, 6.1-6, and 6.1-7 contain summaries of the Federal and state ambient air quality standards and the predicted maximum concentrations for the 300,000 bpcd reference module emissions for Schemes 1, 2, and 3, respectively, at full production capacity. These predictions indicate that levels of sulfur dioxide, particulate matter, nitrogen dioxide, and carbon dioxide arising from the refinery emissions are well below state (also see Appendix 6.1-1) and Federal ambient air quality standards. The predicted three-hour hydrocarbon maximum on all three schemes exceeds the Federal guidelines for hydrocarbon levels under all meteorological conditions. These results are typical for large refinery complexes (RA-119).

TABLE 6.1-5

SCHEME 1$^{(a)}$

SUMMARY OF FEDERAL AND STATE AMBIENT AIR QUALITY STANDARDS AND PREDICTED MAXIMUM CONCENTRATIONS FOR 300,000 BPCD REFINERY EMISSIONS

(Units are micrograms per cubic meter with ppm in parentheses)

	Federal Primary Standard	Federal Secondary Standard	Texas Standard**	Computed Maximum++ Annual Average	Computed Maximum++ 24-Hour Average	Computed Short-Term Maximum++ Unstable Condition	Computed Short-Term Maximum++ Stable Condition	Computed Short-Term Maximum++ Typical Conditions
Sulfur Oxides								
Annual Average (A.M.)$^{(b)}$	80(0.03)			4.2(0.002)				
24-Hr. Maximum*	365(0.14)				26.5(0.01)			
3-Hr. Maximum*		1300(0.5)				135(0.051)	>36^{+++}	36.1(0.014)
30-Minute Maximum			1061(0.4)***			168(0.063)	>45^{+++}	44.9(0.017)
Particulate								
Annual Average (G.M.)$^{(c)}$	75	60		0.7				
24-Hr. Maximum*	260	150			5.1			
5-Hr. Maximum			100			23.0	>6^{+++}	
3-Hr. Maximum			200			25.5	>7^{+++}	
1-Hr. Maximum			400			31.8	>8^{+++}	8.1
Nitrogen Dioxide								
Annual Average (A.M.)	100(0.05)			5.3(0.003)				
Non-Methane Hydrocarbons								
3-Hr. Maximum* (6-9 a.m.)	160(0.24)$^{+}$					1500(2.26)	40000(60.26)	605(0.01)
Carbon Monoxide								
8-Hr. Maximum*	10000(9.)					9.6(0.01)		
1-Hr. Maximum*	40000(35.)					14.6(0.01)		4.4(0.004)

* Not to be exceeded more than once per year.

** Texas standards apply to individual sources and are not to be exceeded at any point at any time.

*** The rescission of this standard for new sources in Brazoria County (and certain other counties) is being considered by the Texas Air Control Board.

$^{+}$ This standard is interpreted by the Texas Air Control Board and by EPA to be a guideline and not a regulation.

$^{++}$ Maximum values are those that occur on or outside the plant boundary.

$^{+++}$ These maxima are beyond the computational range used.

(a) Scheme 1 is for the annual, short-term, and 24-hour computed maximum concentrations.

(b) Arithmetic mean.

(c) Geometric mean.

TABLE 6.1-6

SCHEME 2(a)

SUMMARY OF FEDERAL AND STATE AMBIENT AIR QUALITY STANDARDS AND PREDICTED MAXIMUM CONCENTRATIONS FOR 300,000 BPCD REFINERY EMISSIONS

(Units are micrograms per cubic meter with ppm in parentheses)

	Federal Primary Standard	Federal Secondary Standard	Texas Standard**	Computed Maximum++ Annual Average	Computed Maximum++ 24-Hour Average	Computed Short-Term Maximum++ Unstable Condition	Computed Short-Term Maximum++ Stable Condition	Computed Short-Term Maximum++ Typical Conditions
Sulfur Oxides								
Annual Average (A.M.)(b)	80(0.03)			6.3(0.003)				
24-Hr. Maximum*	365(0.14)				33.1(0.012)			
3-Hr. Maximum*		1300(0.5)				169(0.064)	>45+++	45.1(0.018)
30-Minute Maximum			1061(0.4)***			210(0.079)	>56+++	56.1(0.021)
Particulate								
Annual Average (G.M.)(c)	75	60		1.6				
24-Hr. Maximum*	260	150			9.6			
5-Hr. Maximum			100			43.1	>11.2+++	
3-Hr. Maximum			200			47.8	>13.1+++	
1-Hr. Maximum			400			59.6	>15.0+++	15.2
Nitrogen Dioxide								
Annual Average (A.M.)	100(0.05)			8.0(0.0045)				
Non-Methane Hydrocarbons								
3-Hr. Maximum* (6-9 a.m.)	160(0.24)+					1875(2.85)	50000(75.3)	756.2(1.14)
Carbon Monoxide								
8-Hr. Maximum*	10000(9.)					12.0(0,012)		
1-Hr. Maximum*	40000(35.)					18.2(0.012)		6.9(0.005)

*Not to be exceeded more than once per year.

**Texas standards apply to individual sources and are not to be exceeded at any point at any time.

***The rescission of this standard for new sources in Brazoria County (and certain other counties) is being considered by the Texas Air Control Board.

+This standard is interpreted by the Texas Air Control Board and by EPA to be a guideline and not a regulation.

++Maximum values are those that occur on or outside the plant boundary.

+++These maxima are beyond the computational range used.

(a) Scheme 2 is the same as Scheme 1 except that particulate emissions were increased by 50% and the resulting annual, short-term, and 24-hour maximum concentrations were increased by 50%, 25%, and 25% respectively.

(b) Arithmetic mean.

(c) Geometric mean.

TABLE 6.1-7

SCHEME 3$^{(a)}$

SUMMARY OF FEDERAL AND STATE AMBIENT AIR QUALITY STANDARDS

AND PREDICTED MAXIMUM CONCENTRATIONS FOR 300,000 BPCD REFINERY EMISSIONS

(Units are micrograms per cubic meter with ppm in parentheses)

	Federal Primary Standard	Federal Secondary Standard	Texas Standard**	Computed Maximum++ Annual Average	Computed Maximum++ 24-Hour Average	Computed Short-Term Maximum++ Unstable Condition	Computed Short-Term Maximum++ Stable Conditior	Computed Short-Term Maximum++ Typical Conditions
Sulfur Oxides								
Annual Average (A.M.)$^{(b)}$	80(0.03)			7.35(0.0035)				
24-Hr. Maximum*	365(0.14)				39.8(0.015)			
3-Hr. Maximum*		1300(0.5)				203(0.077)	>54^{+++}	54.2(0.021)
30-Minute Maximum			1061(0.4)***			252(0.094)	>68^{+++}	67.4(0.026)
Particulate								
Annual Average (G.M.)$^{(c)}$	75	60						
24-Hr. Maximum*	260	150						
5-Hr. Maximum			100	1.84		51.8	>13.5^{+++}	
3-Hr. Maximum			200		11.5	57.4	>15.8^{+++}	
1-Hr. Maximum			400			71.6	>18.0^{+++}	18.2
Nitrogen Dioxide								
Annual Average (A.M.)	100(0.05)			9.3(0.005)				
Non-Methane Hydrocarbons								
3-Hr. Maximum* (6-9 a.m.)	160(0.24)$^{+}$					2250(3.39)	60000(90.4)	907.5(1.37)
Carbon Monoxide								
8-Hr. Maximum*	10000(9.)					14.4(0.015)		
1-Hr. Maximum*	40000(35.)					21.9(0.015)		6.6(0.006)

* Not to be exceeded more than once per year.

** Texas standards apply to individual sources and are not to be exceeded at any point at any time.

*** The rescission of this standard for new sources in Brazoria County (and certain other counties) is being considered by the Texas Air Control Board

[+] This standard is interpreted by the Texas Air Control Board and by EPA to be a guideline and not a regulation.

[++] Maximum values are those that occur on or outside the plant boundary.

[+++] These maxima beyond the computational range used.

(a) Scheme 3 is the same as Scheme 1, except that particulate emissions were increased by 50% and the resulting annual, short-term, and 24-hour maximum concentrations were increased by 75%, 50%, and 50%.

(b) Arithmatic mean.

(c) Geometric mean.

The results of the computations demonstrate that the 300,000 bpcd gasoline refinery has little impact on SO_2, particulate, NO_x, and CO ambient concentrations. Therefore, it should be expected that both the 200,000 bpcd fuel oil and gasoline refinery modules that were considered in this study will have a similar minimal impact. The estimated hydrocarbon concentrations exceed the Federal guideline significantly. A similar result is expected for the subject fuel oil and gasoline refineries.

6.1.1.2 Water Quality Impact

Aqueous Effluents

Wastewater will be generated at multiple sources in the refinery module. Table 6.1-8 identifies the major sources in the plant and the species of pollutants present in each. As noted on the table, the various effluents are categorized as process wastes, cooling tower blowdown, or auxiliary refinery systems and wastes. The primary contaminants present in the refinery's wastes include sulfides, ammonia, phenols, oil, dissolved and suspended solids, biochemical oxygen demand (BOD), and chemical oxygen demand (COD). Under existing Federal limitations, discharge of the above wastes will not be permitted.

Water management can exercise a number of strategies through direct implementation of the wastewater treatment processes. There are four types of applicable wastewater treatments: in-plant; primary; secondary; and tertiary. The degree to which each of these processes is utilized depends on the local area discharge regulations, the quality of wastewater effluents prior to treatment, and the degree of recycle or reuse of water. A summary of pollutant types contained in the refinery module wastewater streams is presented in Table 6.1-9.

TABLE 6.1-8

SUMMARY OF REFINERY WASTEWATER EFFLUENTS AND APPLICABLE TREATMENTS

Waste Source	Major Pollutant Present								Applicable Treatments			
	H_2S	NH_3	Phenols	Oil	Dissolved Solids	Suspended Solids	BOD	COD	In-Plant[d]	Primary Treatment	Secondary Treatment	Tertiary Treatment
A. Process Wastes												
1. Crude Desalting			X	X	X		X	X		X	X	X
2. Atmospheric Distillation	X	X	X	X			X	X	X	X	X	
3. Pentane Deasphalting				X			X	X		X	X	
4. Deasphalted Oil HDS	X	X		X			X	X	X	X	X	
5. Partial Oxidation	X	X		X	X		X	X	X	X	X	X
6. Hydrocracking	X	X		X			X	X	X	X	X	
7. Fluid Catalytic Cracking	X	X	X	X			X	X	X	X	X	
8. HF Alkylation	X		X	X			X	X	X	X	X	
9. Sulfur Recovery (Tail Gas Treating Unit)	X								X			
B. Refinery Cooling System[a] (cooling tower)					X							X
C. Auxiliary Refinery Systems and Wastes												
1. Steam Generation					X							X
2. Electric Power Generation					X							
3. Sanitary Wastes[b]						X	X				X	X
4. Precipitation Runoff[c]				X		X	X	X		X		
5. Water Treatment Wastes					X	X				X		X
6. Miscellaneous Operations				X	X	X	X	X		X	X	

---

[a] Cooling tower operating at 20 cycles of concentration.

[b] Represents refinery sanitary waste, only.

[c] Includes runoff from process and tank farm areas, only.

[d] Refers to sour water stripper.

SOURCE: (BE-147, AM-041, RA-181)

TABLE 6.1-9

APPROXIMATE COMPOSITION OF REFINERY EFFLUENT AT THE OUTFALL

AQUEOUS EFFLUENT CONSTITUENT	200,000 BPCD FUEL OIL REFINERY MODULE	200,000 BPCD GASOLINE REFINERY MODULE	300,000 BPCD GASOLINE REFINERY
BOD, ppm	15	15	<20
COD, ppm	80	80	<80
Ammonia, ppm	2	2	< 2
H_2S, ppm	0.1	0.1	0.1
Total Phosphorous (as PO_4), ppm	2	2	190
Phenols, ppm	0.1	0.1	0.1
Oil and Grease, ppm	2	2	2
Suspended Solids, ppm	10	10	10
Dissolved Solids, ppm	370	370	15,000
Total Nitrogen (as NO_3), ppm	-	-	230
Mercaptans, ppm	-	-	None
Flow, million gallons/day	3	3	0.25*

*Cooling tower blowdown.

SOURCE: (RA-181)

The wastewater treatment processes assumed for the 200,000 bpcd fuel oil and gasoline refinery modules consist of in-plant waste treatment, primary waste treatment, and a high-efficiency secondary waste treatment (such as activated sludge). The 300,000 bpcd gasoline refinery reference module has the same water treating facilities plus a tertiary treatment unit. Also, the aqueous effluents of the reference module are treated and circulated to the cooling tower, as shown in Figure 6.1-7. In-plant, primary, and secondary treatments are utilized to meet existing effluent limitations. Tertiary treatment, in the form of water desalination processes, is typical of facilities that will be required to meet the minimal effluent limitations proposed for 1985.

The comparatively large concentrations of total phosphorus, dissolved solids, and total nitrogen in the 300,000 bpcd reference refinery as shown in Table 6.1-9 are due to the recycle of treated wastewater back into the refinery cooling tower. The resulting effluent stream consists entirely of the cooling tower blowdown and has much less volumetric flow than the effluent from the 200,000 bpcd gasoline refinery module which does not practice the recirculation technique.

Effluents from the three refinery modules are assumed to have the composition shown in Table 6.1-9; the actual composition of wastewater discharged to the receiving stream may differ somewhat from that shown, depending on final process configuration and design. This difference is not anticipated to be great and no significant change in the water impact assessment is expected.

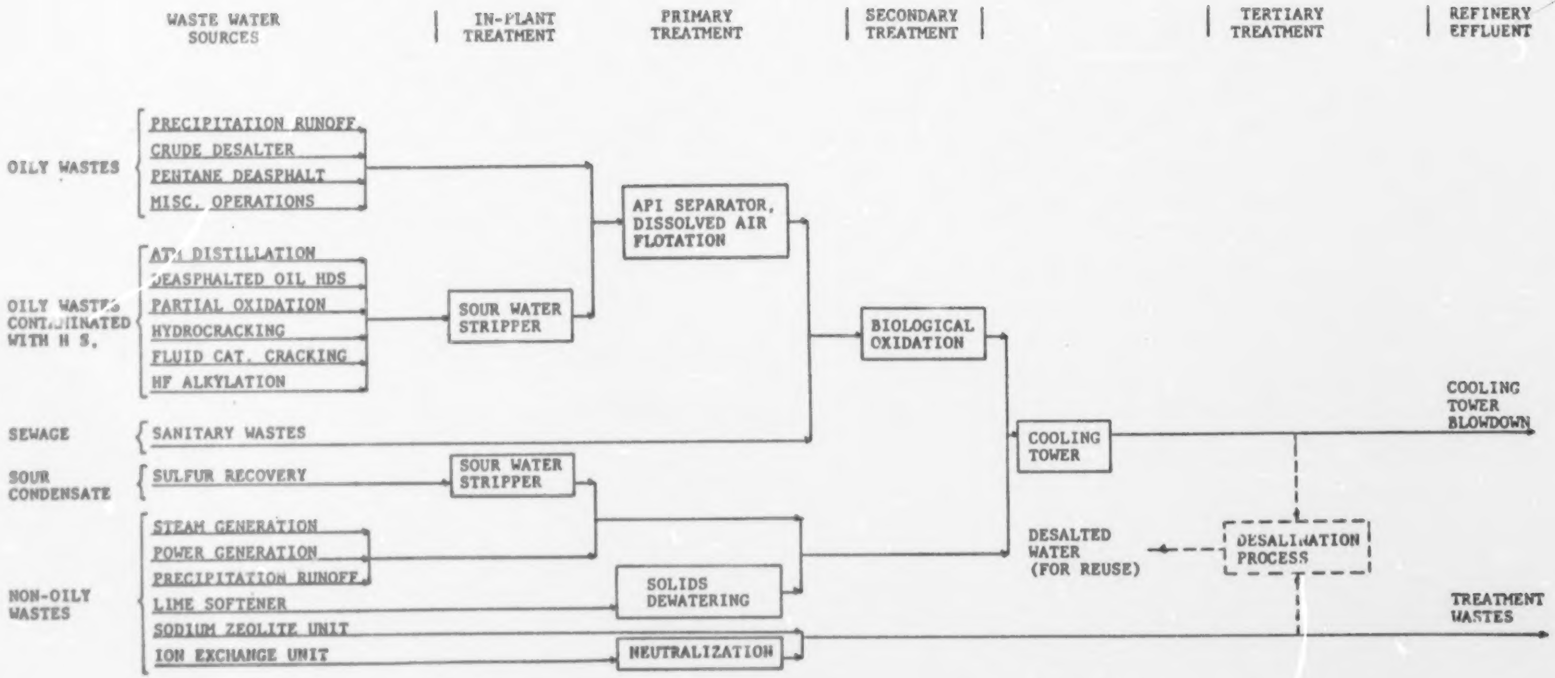

WASTE WATER SOURCES
IN-PLANT TREATMENT
PRIMARY TREATMENT
SECONDARY TREATMENT
TERTIARY TREATMENT
REFINERY EFFLUENT
OILY WASTES
PRECIPITATION RUNOFF
CRUDE DESALTER
PENTANE DEASPHALT
MISC. OPERATIONS
OILY WASTES CONTAMINATED WITH H S.
ATM DISTILLATION
DEASPHALTED OIL HDS
PARTIAL OXIDATION
HYDROCRACKING
FLUID CAT. CRACKING
HF ALKYLATION
SEWAGE
SANITARY WASTES
SOUR CONDENSATE
SULFUR RECOVERY
NON-OILY WASTES
STEAM GENERATION
POWER GENERATION
PRECIPITATION RUNOFF
LIME SOFTENER
SODIUM ZEOLITE UNIT
ION EXCHANGE UNIT
SOUR WATER STRIPPER
SOUR WATER STRIPPER
API SEPARATOR, DISSOLVED AIR FLOTATION
SOLIDS DEWATERING
NEUTRALIZATION
BIOLOGICAL OXIDATION
COOLING TOWER
DESALTED WATER (FOR REUSE)
DESALINATION PROCESS
COOLING TOWER BLOWDOWN
TREATMENT WASTES

FIGURE 6-7 PROPOSED WATER MANAGEMENT PLAN

By comparison, the "reference" module effluent has a much higher concentration of total phosphorous (PO_4) and dissolved solids, though its flow rate is just 1/12 of the discharge rate of either of the other two refinery modules in this study. Furthermore, the "reference" module effluent contains detectable amounts of nitrogen (NO_3). The main differences can be attributed to the fact that the "reference" module is much larger and that it circulates the treated water to the cooling tower. This recycle and reuse of water gives rise to the higer content of dissolved solids in these effluent. Therefore, to promote water use efficiency, the EPA has placed no restriction on total dissolved solids in either its effluent limitation guidelines or new source performance standards.

The oxygen-demanding material in the effluent (represented by COD, BOD, ammonia, and sulfide) are probable maximum values, in that an indeterminant amount of oxidation will occur upon aeration in the cooling tower. The concentrations shown are conservative-case estimates for the blowdown. In the case of the two refinery modules, the effluent discharge rate is estimated at 15 gallons per barrel of oil throughput.

Water Quality Modeling

The water quality impact of industrial pollutants is usually directly related to the concentrations in which they are present in receiving waters. It is, therefore, necessary to determine the pollutant concentrations in waters receiving refinery effluent discharges. Once the effluent concentrations are known, they can be compared to pre-existing ambient levels, to levels known to be harmful, or to government regulations to assess their overall water quality impact.

Mathematical models are useful tools in computing the pollutant concentrations in receiving waters which result from predicted refinery effluent discharges. Two levels of complexity are exhibited by the models. A very simple model is used to predict pollutant concentrations. This model gives background concentrations that are some distance from the effluent outfall and applies to well mixed streams. The other model, in addition to giving background concentrations, computes constant-concentration contours - extending from effluent outfall to the region of background concentrations. This model is especially useful in showing pollutant distributions in tidal waters during conditions of flood, slack, and ebb tides. A detailed discussion of the two types of models is presented in Appendix 6.1-2.

The data required for modeling includes the effluent pollutant concentrations and effluent flow rates predicted for a refinery module; and flow rates, tidal conditions, and configuration for the receiving water body. The behavior of water bodies varies widely throughout the U.S. In order to obtain meaningful computed pollutant concentrations in the receiving water, it is important to define as accurately as possible the point of condition of the waters receiving the refinery effluent at the release.

Dispersion of Refinery Effluents

The dispersion of the effluents from the "reference" refinery are considered for example purposes. In this case, the effluents are discharged into a river at a point some twenty miles from its mouth on the Texas Gulf Coast. The river is influenced by diurnal tides. The bottom of the river is below mean sea level, and is subject to saline water incursion. Both the tidal effect and the incursion are more significant at low stream flow conditions.

The discharge of the effluent increases the total dissolved solids content of the river by about 70 ppm at median flow conditions. This is a nominal increase of one percent. The dispersion of non-conserved pollutants can be illustrated by the calculate effect on dissolved oxygen (DO) concentration shown in Figure 6.1-8. The calculation is made on the seven day - ten year low flow condition. The localized DO depression is five percent of the saturation value.

These are the results of one example. Another study (RA-119) considered the siting of large new refineries at five U.S. Coastal sites. In all cases, very little impact was predicted. With full implementation of presently available technology, refineries can be designed for minimal impact on receiving waters.

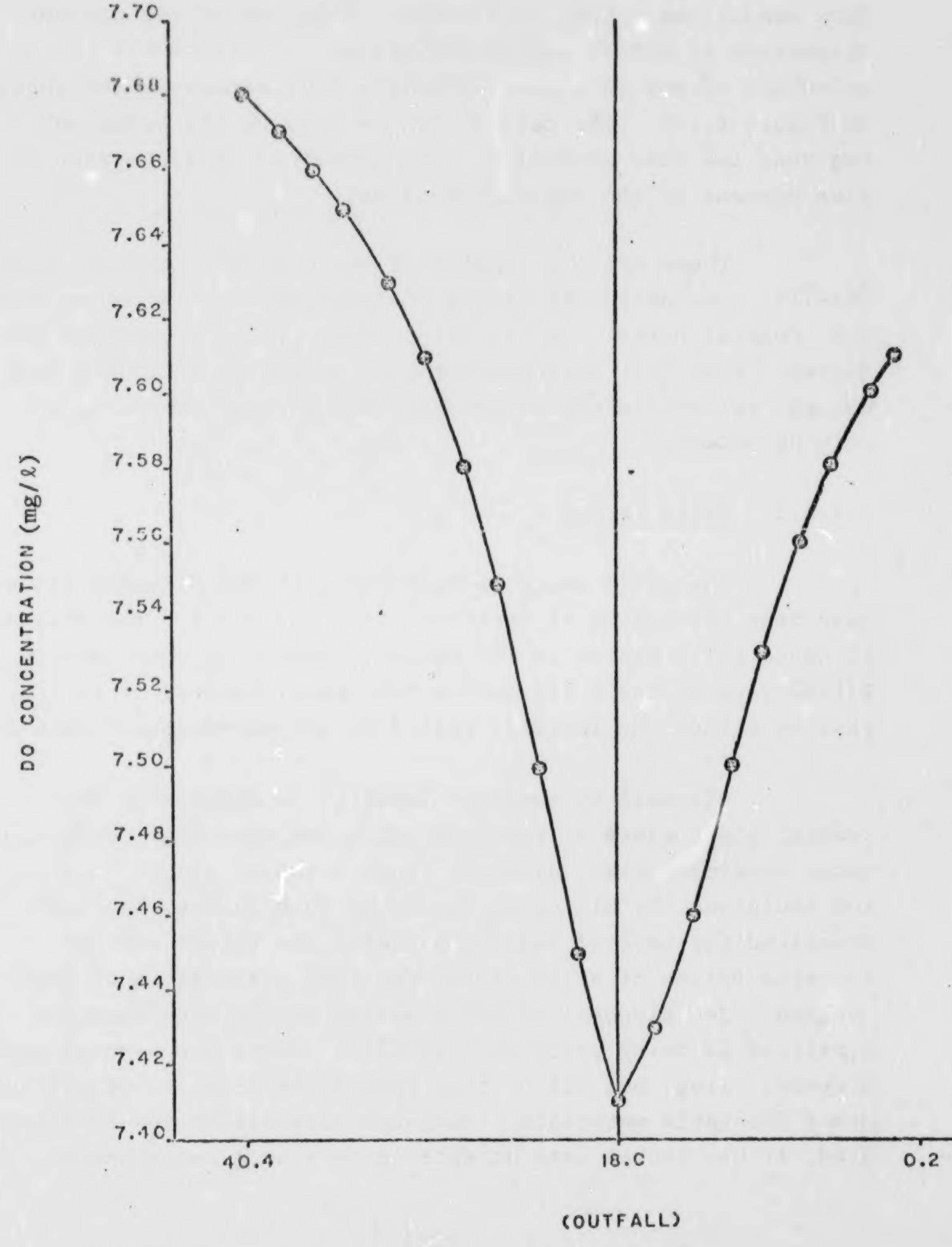
6.1.1.3 Solid Wastes

The solid wastes associated with the refinery processing have been identified in Sections 3.1.3 and 3.2.3. The disposal of these solid wastes is the primary concern in this section. Refinery-generated solid wastes have been disposed of in the past by either the landfill method or the sea disposal technique.

Disposal by sanitary landfill is applicable for all general plant waste as received, with the exception perhaps of water treatment plant sludges. Land disposal of oily sludges and emulsions, by mixing at depths up to 6 inches, has been practiced for several years (BE-228). The nature and the sizeable volume of solid wastes for land disposal is of great concern. Sea disposal of solid wastes having high specific gravities is being practiced (BE-228). There are several approved disposal sites, but all of them forbid the disposal of oil and other floatable materials. Although disposal at sea is being used, it has become less acceptable on a long range basis.

FIGURE 6.1-8 DISSOLVED OXYGEN CONCENTRATION PROFILE.

RIVER FLOW = 4.09 CFS
T = 27° C
C_{SAT} = 7.7 mg/ℓ



Incineration of solid wastes, while acceptable, is not an ultimate disposal method. The disposal of the incinerated solid waste and their effects on petroleum refinery siting are discussed in this section.

An anticipated on-site incineration unit for oily solids and other organic sludges, as well as for much of the office, shop, and other non-processing refuse, will reduce considerably the volume of material to be disposed of. The resulting incinerator ash, in addition to discarded catalyst, will require some type of ultimate disposal.

The hydrology and geology of the site are basic considerations for solid waste disposal sites. Ideally, geological materials at the site must possess the necessary impermeability characteristics, with hydraulic conductivities below 10^{-6} cm/sec. Also, water-transmitting material and groundwater levels must not be encountered at any depth.

Another prerequisite in selection of a solid waste disposal site is assurance that the site will not be flooded. (This denies a potential source of water to form leachate, and also avoids possible erosion of the cover material.) The site should be located within the flood-protection levee of the refinery if within general proximity of a flood zone.

In general, all problems pertaining to hydrology, geology, and potential flooding nature of a dump site, covering periods both during and after the operational life of the refinery, must be studied as part of any refinery siting program.

6.1.2 Raw Material Availability

Raw material availability presents a unique set of environmental impact problems and problems associated with petroleum refinery siting. Raw material refers to both feedstock and water. Their implications in this study are discussed in the following sections.

6.1.2.1 Feedstock Availability

Feedstock for petroleum refineries may come from either foreign of domestic sources. In 1973, the United States crude oil and lease condensation production averaged 9.2 million barrels per day, and 3.2 million barrels of crude per day were imported (AM-099). These crude oil supplies served as feedstocks to the 247 operational petroleum refineries in the U.S. (OI-008). The feedstocks reached the refineries through various means of transportation. Thus, feedstock availability is related to the mode of transportation, and its relationship to refinery siting is discussed below.

Foreign Source

Feedstock from abroad creates some environmental impact problems at U.S. port facilities. The chance of major oil spills is one problem. Tanker sizes are in some measure related to the problem.

Proposed petroleum refineries that will receive their crude oil supply from abroad are likely to be sited near coastal waters. As for the economics of feedstock, previous studies indicate that larger tankers carrying vast amounts of crude oil offer cost advantages (US-124). Tankers being considered are in the very large crude carrier (VLCC) class, i.e., 250,000 DWT and ultra large crude carrier (ULCC) class, i.e., about 400,000 DWT. These tankers cannot be received by the existing U.S. ports as indicated in Table 6.1-10. Figure 6.1-9 shows the geographical location of selected U.S. ports. Thus, a problem exists for imported feedstock. However, this problem can be resolved through the development of strategic superport facilities, such as offshore deepwater-terminals or the dredging of harbor channels. Figure 6.1-9 also indicates the regional location of potential ports for supertankers. This development of superport facilities will have a potential environmental impact. Of the two superport facilities mentioned above, the construction of offshore deepwater-terminals would have a less adverse environmental impact than dredging or the use of existing port facilities (PR-074). The President's Energy Message on April 18, 1973, stated (PR-074).

> "The environmental advantage of offshore deepwater ports is that they reduce the risks of collision and grounding and minimize the probability that spilled oil will reach beaches or estuaries. The most valid environmental concern involves the impact of primary and secondary economic development, such as refineries and petrochemical plants, associated with the port. These risks are recognized and can be controlled through land use planning and adequate local zoning. Dispersion of facilities versus concentration with only a few ports would probably significantly reduce the environmental impact on any particular region".

The 1972 Council on Environmental Quality (CEQ) made preliminary assessments on the probable environmental impact of the operation of ports for supertankers and they are discussed in Reference US-124.

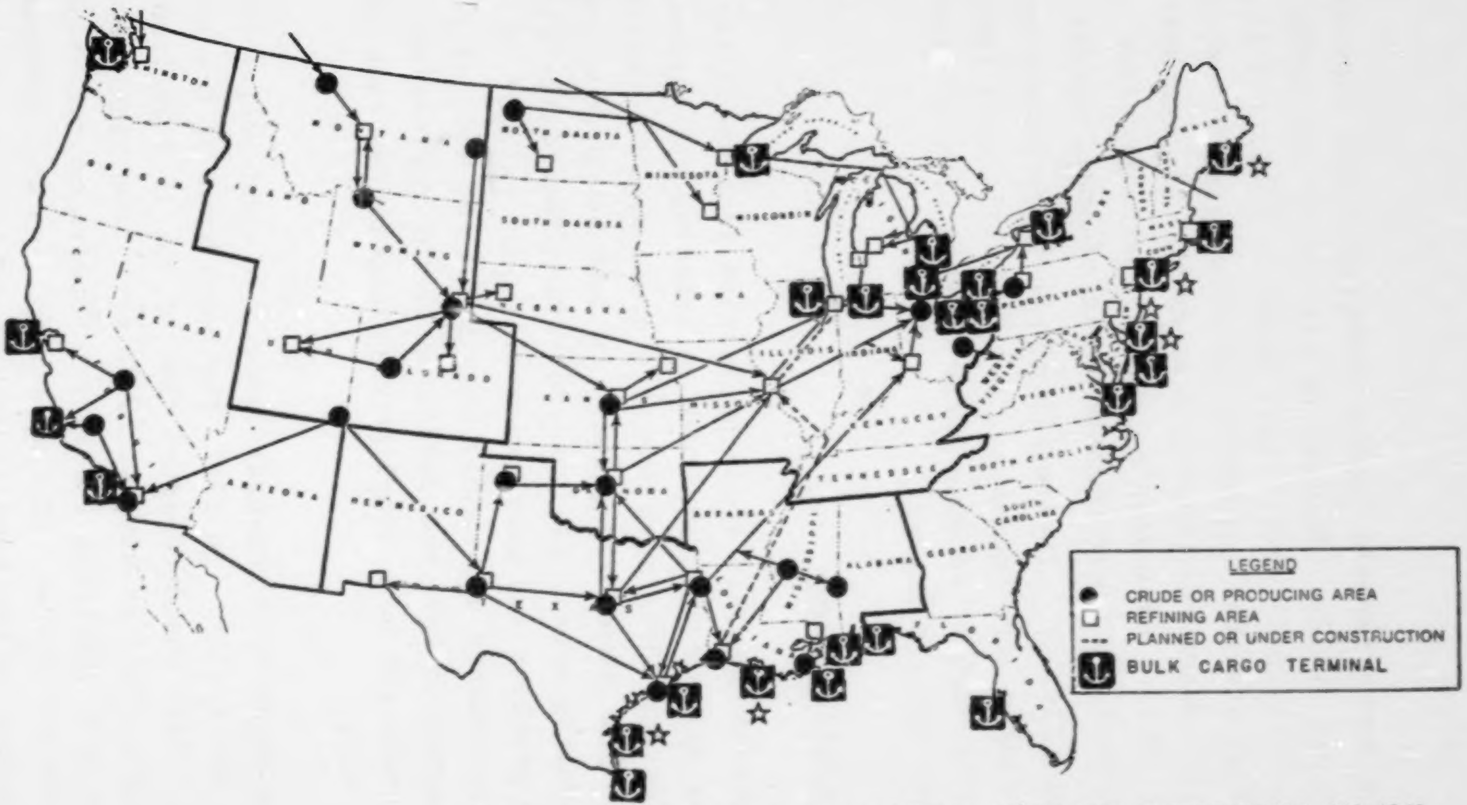
TABLE 6.1-10

SELECTED U.S. PORTS HANDLING SIGNIFICANT AMOUNTS OF BULK CARGO

	Controlling Depth (feet)	Est. Maximum Permissible Vessel Size When Fully Loaded (dwt.)
EAST COAST		
Delaware River ports	40	53,000
Hampton Roads, Va.	45	80,000
New York, N.Y.	35	40,000
Portland, Me.	45	80,000
Baltimore, Md.	42	53,000
Boston, Mass.	40	40,000
GULF COAST		
New Orleans, La.	40	50,000
Tampa, Fla.	34	35,000
Baton Rouge, La.	40	50,000
Mobile, Ala.	40	45,000
Corpus Christi, Tex.	45	50,000
Houston, Tex.	40	50,000
Brownsville, Tex.	36	30,000
Pascagoula, Miss.	38	35,000
PACIFIC COAST		
Long Beach, Calif.	52	150,000
Los Angeles, Calif.	51	150,000
San Fran. Bay ports, Calif.	35	40,000
Seattle, Wash.	73	250,000
GREAT LAKES		
Chicago, Ill.	28	10,000
Indiana Harbor, Inc.	29	12,000
Detroit, Mich.	29	12,000
Duluth/Superior, Minn./Wis.	32	12,000
Buffalo, N.Y.	29	12,000
Ashtabula, Ohio	29	12,000
Cleveland, Ohio	29	15,000
Conneaut, Ohio	27	13,000
Toledo, Ohio	28	12,000

Source: (US-124)

CRUDE OIL PIPELINES


LEGEND
● CRUDE OR PRODUCING AREA
□ REFINING AREA
--- PLANNED OR UNDER CONSTRUCTION
⚓ BULK CARGO TERMINAL
WASHINGTON
OREGON
IDAHO
MONTANA
WYOMING
NEVADA
COLORADO
ARIZONA
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
WISCONSIN
IOWA
ILLINOIS
INDIANA
MISSOURI
ARKANSAS
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
NORTH CAROLINA
SOUTH CAROLINA
VIRGINIA
PENNSYLVANIA
NEW YORK
MAINE

☆ REGIONAL LOCATION OF THE POTENTIAL PORTS FOR SUPERTANKERS (US-124)

FREEPORT, TEXES (2 SITES)
MISSISSIPPI DELTA, LOUISIANA (2 SITES)
OUTSIDE DELAWARE BAY (2 SITES)
DELAWARE BAY (INSIDE)

NEW YORK BIGHT, NEW YORK-NEW JERSEY (2 SITES)
RARITAN BAY, NEW JERSEY
MACHIAS BAY, MAINE

FIGURE 6.1-9

The environmental impact associated with imported feedstock is oil spills. Sources of oil spills are ports and tankers. Oil spill statistics, given in Table 6.1-11, explicitly indicate that terminals and ships are the two major contributors to water pollution. A study on the probability of large oil spills, estimated by vessel class, provides some insight into the environmental merit of small versus large tankers (US-124). The result of the study points out that as the tanker size increases, the probability of large spill decreases, mainly because large tankers have a lesser number of port calls per year.

Domestic Source

Current domestic crude production is essentially all designated as part of the feedstock to existing refineries. New refineries depending upon domestic crude would necessarily be related to new crude production. If this new production is from new producing areas, new transportation facilities will be needed. The problems and environmental impact related to domestic crude sources are mainly charged to the mode of transportation elected to move the feedstock to the refineries. Movement of crude can be accomplished by pipelines, tank barges, or rail tank cars.

The major environmental concern in crude oil transportation is oil spills. In 1972, the Department of Transportation and U.S. Coast Guard reported that of the 18.8 million gallons of oil spilled on waters, 19.9% came from tank barges and 6.6% came from pipelines (US-159). Reports on rail tank cars oil spills are sparse. Oil spills on land will eventually reach water bodies in the form of nondegradable organics (HI-090), which amount to about 5% of the total quantity of oil spilled.

TABLE 6.1-11

OIL SPILL STATISTICS (BARRELS)

Type of Spill	1971	1972
Petroleum Industry Related Spills		
Terminal		
Number	1,475	1,632
Volume	125,800	54,700
Ships (offshore)		
Number	22	32
Volume	400	51,600
Offshore Production Facilities		
Number	2,452	2,252
Volume	15,600	5,700
Onshore Pipeline		
Number	74	162
Volume	8,700	29,300
Total		
Number	4,023	4,078
Volume	150,500	141,300
All Spills		
Number	7,461	8,287
Volume	205,000	518,000

Source: (FE-076) and

The Massachusetts Institute of Technology Department of Ocean Engineering, 1974, "Analysis of Oil Spill Statistics", prepared for the Council on Environmental Quality under Contract No. EQC330, using U.S. Coast Guard data.

6.1.2.2 Water Availability

Water is essential to almost every facet of energy conversion processes. The extraction of fuel resources, fuel preparation, transportation of fuels, utilization of fuels to generate energy, and disposal of waste products in an environmentally acceptable manner involve water. The need for water varies with the source of energy, region of development, and degree of complexity of environmental control.

Table 6.1-12 gives the major uses of water for various forms of energy processes. Note in the table that refineries' water requirement is 43 gallons per barrel or 7.58 gallons per million Btu's, mainly as process and cooling water. For example, a 300,000 bpcd gasoline refinery will require as much as 13 million gallons of water per day for its operation. This is a substantial quantity of water. It is a critical factor in selecting the refinery site.

In general, the Mississippi River divides the relatively humid east coast from the more arid western U.S. Some western areas (notably the northwest) have heavy rainfall, but by and large, the western central states are a relatively arid region. Figure 6.1-10 shows the relative water abundance or deficit across the U.S. (US-083). Water abundance means that annual rainfall exceeds evaporation losses. For deficits, evaporation losses exceed rainfall.

Figure 6.1-11 gives a general impression of the sizes and locations of major rivers in the U.S. The western central states do not have an abundant, large river water supply. Production facilities in these areas are presently being considered that would require water at rates exceeding reliable natural water supply at the facility site. Therefore, elaborate schemes are being studied for bringing the water to the facilities.

TABLE 6.1-12

WATER USED FOR ENERGY

(Source: FE-076)

Energy Source	Standard Unit	Consumption Demand For Water	Water Needed Gal/10^6 BTU	Major Uses Of Water
Western coal mining	ton	6-14.7 gal/ton	0.25 - 0.61	Dust Control Coal Washing
Eastern surface mining	ton	15.8-18.0 gal/ton	0.66 - 0.75	Dust Control Coal Washing
Eastern surface mining	ton			Dust Control Coal Washing
Oil shale	barrel	145.4 gal/bbl	30.1	Mining, cooling, oil shale disposal preparation
Coal gasification	MSCF	72-158 gal/MSCF	72 - 158	Process use Cooking use
Coal liquefaction	barrel	175 - 1,134 gal/bbl	31 - 200	Process use Cooking use
Nuclear	Kwh	0.80 gal/Kwh	234.46	Cooling, uranium mining
Oil and gas production	barrel	17.3 gal/bbl	3.05	Well drilling, secondary and tetiary recovery
Refineries	barrel	43 gal/bbl.	7.58	Process H_2O Cooling H_2O
Fossil fuel power plants	Kwh	0.41 gal/Kwh	120.16	Cooling H_2O
Gas processing plants	MSCF	1.67 gal/MSCF	1.67	Cooling H_2O

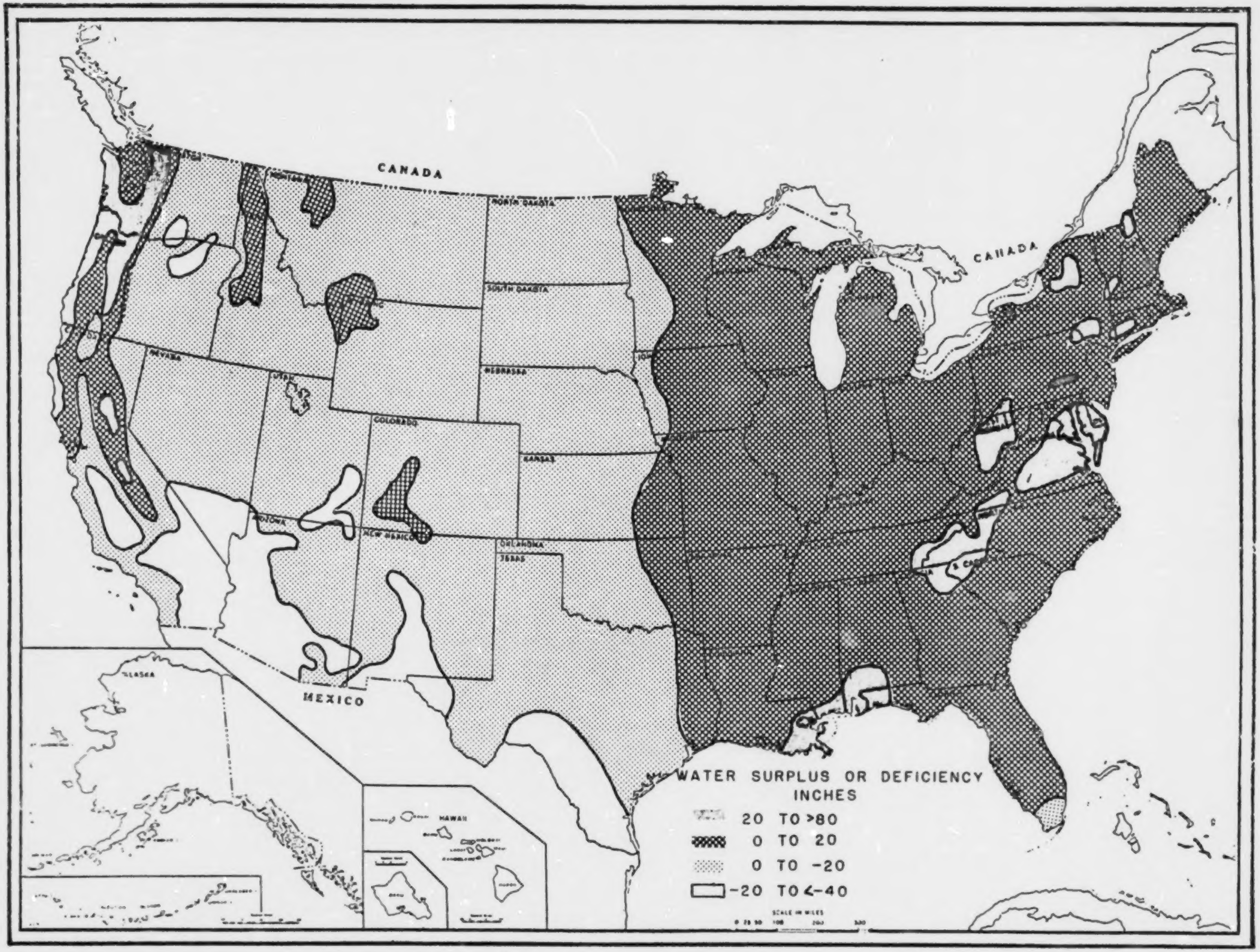

CANADA
CANADA
MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
COLORADO
NEW MEXICO
ARIZONA
UTAH
NEVADA
MONTANA
ALASKA
HAWAII
WATER SURPLUS OR DEFICIENCY
INCHES
20 TO >80
0 TO 20
0 TO -20
-20 TO <-40
SCALE IN MILES

FIGURE 6.1-10   RELATIVE WATER ABUNDANCE OR DEFICIT ACROSS THE U.S.

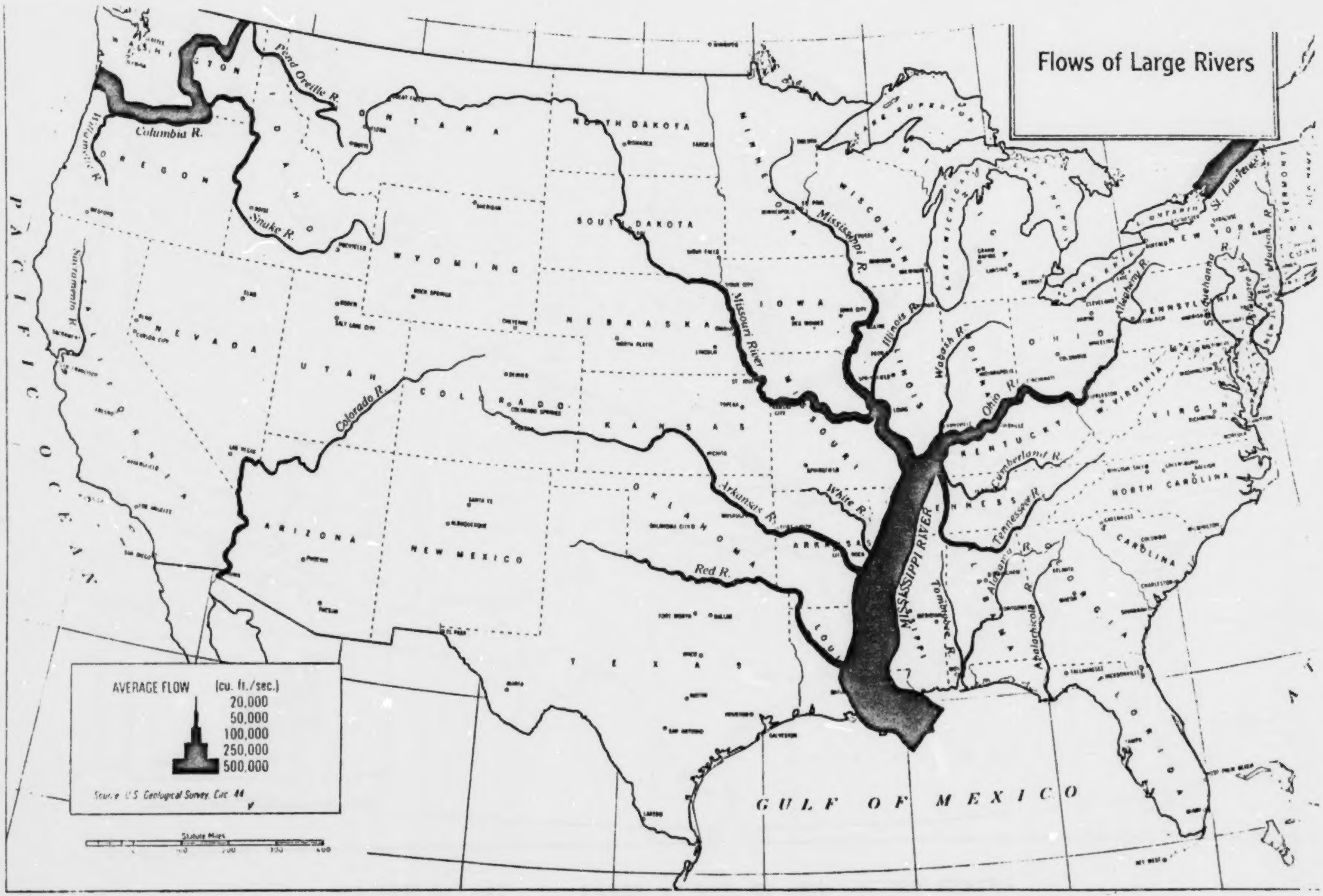

Flows of Large Rivers
AVERAGE FLOW
(cu. ft./sec.)
20,000
50,000
100,000
250,000
500,000
Source U.S. Geological Survey, Circ. 44
Statute Miles
PACIFIC OCEAN
GULF OF MEXICO
Columbia R.
Willamette R.
Pend Oreille R.
Snake R.
Sacramento R.
Colorado R.
Missouri River
Mississippi R.
Illinois R.
Wabash R.
Ohio R.
MISSISSIPPI RIVER
Arkansas R.
White R.
Red R.
Cumberland R.
Tennessee R.
Tombigbee R.
Alabama R.
Apalachicola R.
Allegheny R.
Susquehanna R.
Delaware R.
Hudson R.
St. Lawrence R.
WASHINGTON
OREGON
IDAHO
MONTANA
WYOMING
NEVADA
UTAH
COLORADO
ARIZONA
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
ILLINOIS
MICHIGAN
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
WEST VIRGINIA
PENNSYLVANIA
NEW YORK
NEW JERSEY
VERMONT
LAKE SUPERIOR
LAKE MICHIGAN
LAKE HURON
LAKE ERIE
LAKE ONTARIO

FIGURE 6.1-11 LARGE RIVERS OF THE UNITED STATES

Water laws and regulations are also important factors in refinery siting. The Federal Energy Administration's (FEA) Project Independence Report (FE-076) indicates that the availability of water in any area is governed partly by Federal actions, but more importantly by physical conditions and by state and local prerogatives. Also, the report stresses four factors that determine availability:

(1) Runoff - Some regions have inadequate rainfall and runoff to meet the demands of all water users.

(2) Institutional Factors - Federal and state laws, Indian water rights, interstate compacts, and international treaties govern the allocation of water to the different users.

(3) Environmental Considerations - The Federal Water Pollution Control Act Amendments, regulating thermal pollution, sedimentation and acid runoff from strip mining, increases in salinity, salt water intrusion, and coastal water quality affect water availability.

(4) Capital Investment and Repayment - Construction of water supply projects for energy activities may be impeded by debt limitations and failures in authorizing bond issues.

The second factor is of direct consequence in this report.

The major constraints in water use in some regions of the U.S. are primarily political. There are legal agreements between the Federal government, the individual states, and the river basin authorities which interplay throughout the whole water availability question. A brief summary of the major laws, namely the Law of River Compacts, State Water Laws, and Federal Water Laws are discussed in Appendix 6.1-3.

6.1.3 Product Transportation

In siting a petroleum refinery, it is important to consider the facilities that are available for reaching the market. These facilities fall in the area of product transportation. There are three major modes of product transportation; railroad, waterway, and pipeline.

Railroad

The environmental impact of rail transportation for petroleum products can be charged to air emissions (mainly hydrocarbon) and liquid product spills. These constitute relative small factors in refinery, SNG, or LNG siting considerations.

Waterways

In this country, domestic waterway systems include barge movements on the inland and intercoastal waterways and ship movements on the Great Lakes and on the oceans. Figure 6.1-12 shows the U.S. waterway system. Nearly half of all petroleum and petroleum products are transported by means of this waterway system. Environmental consequences from water transportation system are attributed to spills. Statistics for 1972 on polluting incidents in and around U.S. waters indicate that

WATERWAYS OF THE UNITED STATES

(SOURCE: FE-076)

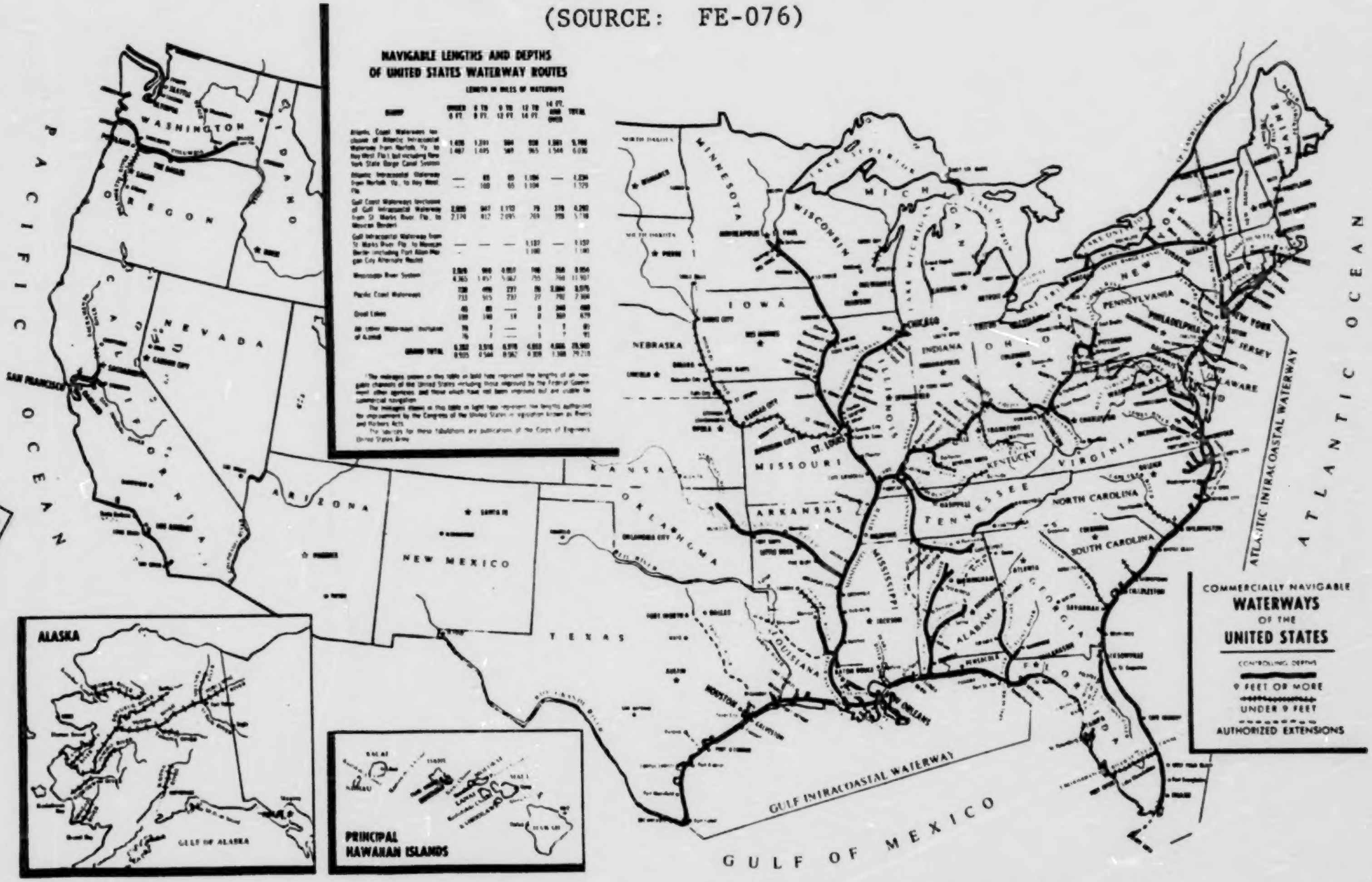

NAVIGABLE LENGTHS AND DEPTHS OF UNITED STATES WATERWAY ROUTES
PACIFIC OCEAN
ATLANTIC OCEAN
GULF OF MEXICO
ATLANTIC INTRACOASTAL WATERWAY
GULF INTRACOASTAL WATERWAY
WASHINGTON
OREGON
IDAHO
CALIFORNIA
NEVADA
ARIZONA
NEW MEXICO
TEXAS
OKLAHOMA
KANSAS
NEBRASKA
NORTH DAKOTA
SOUTH DAKOTA
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
MISSISSIPPI
WISCONSIN
MICHIGAN
ILLINOIS
INDIANA
OHIO
KENTUCKY
TENNESSEE
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
PENNSYLVANIA
NEW YORK
NEW JERSEY
MAINE
SAN FRANCISCO
ST. LOUIS
CHICAGO
NEW ORLEANS
HOUSTON
PHILADELPHIA
ALASKA
GULF OF ALASKA
PRINCIPAL HAWAIIAN ISLANDS
COMMERCIALLY NAVIGABLE
WATERWAYS
OF THE
UNITED STATES
CONTROLLING DEPTHS
9 FEET OR MORE
UNDER 9 FEET
AUTHORIZED EXTENSIONS

FIGURE 6.1-12

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light petroleum products were responsible for 35% of the total spills while heavy oils accounted for 9% (US-159).

Pipelines

The U.S. oil pipeline network consisted of 170,000 miles by the end of 1973 (IN-047), with 38% dedicated to product transport and the remaining 62% to crude gathering and trunk lines. The locations of the product lines in the U.S. are shown in Figure 6.1-13. These pipelines interconnect existing petroleum refineries and the major markets. New refineries will require new feedstock and product pipelines. The main environmental concern with petroleum product transportation by pipeline is spills. The impacts of these spills on soil are not currently well defined.

PRODUCT PIPELINES

(SOURCE: FE-076)

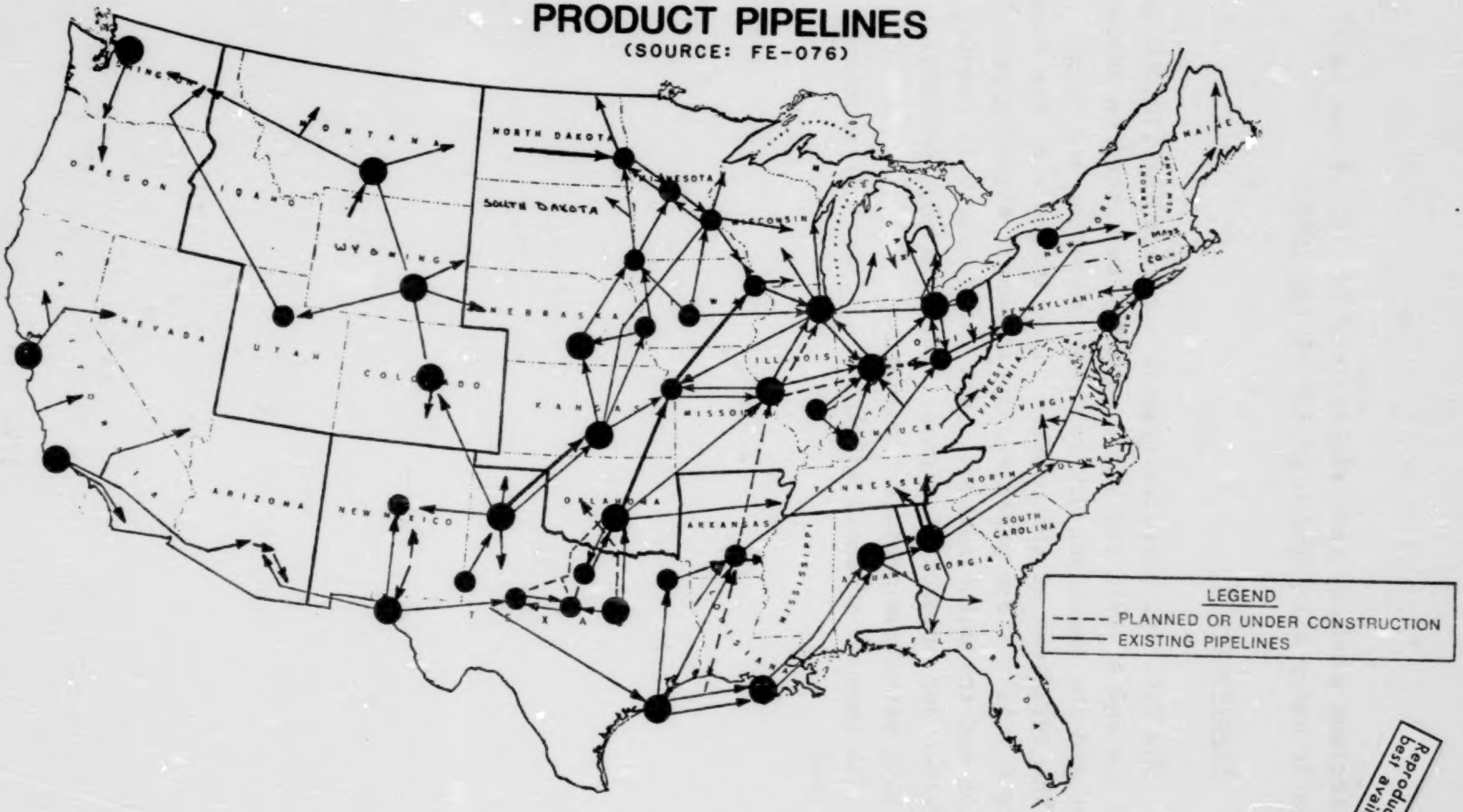
LEGEND
PLANNED OR UNDER CONSTRUCTION
EXISTING PIPELINES
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
COLORADO
ARIZONA
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
ILLINOIS
MICHIGAN
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
WEST VIRGINIA
PENNSYLVANIA
NEW YORK
VERMONT
NEW HAMPSHIRE
MAINE
MASS.
CONN.

FIGURE 6.1-13

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6.2 SNG Plant Impact

There is limited production of SNG in the U.S. In the U.S. today a principal technique of producing SNG is through gasification of naphtha and lighter petroleum fractions. Gasification of other feestocks such as middle distillates, gas oil, crude oil and coal, can also produce SNG.

The design, construction, and operation of SNG plants must comply with Federal environmental legislation and regulations concerning air quality (Air Quality Act, 42 U.S.C.A. 1857, 40 C.F.R. 50, et seq.), and with the Federal Water Pollution Act of 1972, the Solid Waste Disposal Act, and the Rivers and Harbors Act of 1899 (The Refuse Act).

This section deals with the example of siting naphtha-based SNG plants of the 125 MM scfd capacity class, operating with the Catalytic Rich Gas (CRG) process. The CRG process is discussed in Section 2.3. Environmental impacts and problems associated with SNG plant siting are described in terms of effluents (air and water emissions), raw materials (feedstock and water requirements), product transportation, and the existing laws (Federal, state, and local) that interact with these parameters. The approach to the analysis is similar to the scheme that was used in the discussion of petroleum refinery siting presented in the preceding section.

6.2.1 SNG Plant Effluents

Effluents of main concern from an SNG plant employing the CRG process are air emissions and liquid effluents. There are essentially no solid wastes from an SNG plant with this type of process other than spent catalysts (FE-084). The spent catalysts can be returned to the catalyst vendors for reclaiming of valuable metals.

Environmental effects of air emissions and liquid effluents from an SNG plant are assessed from the standpoint of ambient air quality and water quality.

6.2.1.1 Air Emissions Impact

The major air emissions from SNG plants are particulates, sulfur dioxide (SO_2), hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x). Estimated air emissions from the 125 MM scfd SNG plant module described in Section 3.4 are summarized in Table 6.2-1 along with the air emissions of the 300,000 bpcd refinery "reference" module. Table 6.2-1 explicitly indicates that SNG plant air emissions are by far smaller than those of the refinery "reference" module, by factors ranging from 9 to 240.

In order to quantify the impact of the air emissions on the ambient air quality of a site, it is necessary to compute the downwind maximum concentrations of the pollutants for a given set of data. This data would include stack parameters, plant configuration, and meteorological data of the site. If this information is available, the maximum concentrations can easily be computed by employing air dispersion models. The impact of the SNG plant on the ambient air quality of a site can be described through logical comparative analysis with the impact of the refinery "reference" module which was discussed in Section 6.1.1.1.

To establish a meaningful comparison, it must be assumed that the stack parameters, basic plant configuration, and meteorological data that were used for the refinery "reference" module analysis also apply to the SNG plant module. In addition, Schemes 1-3 that were discussed and summarized in Table 6.1-4

TABLE 6.2-1

AIR EMISSIONS - SNG MODULE COMPARISONS

Pollutant	125 MM scfd SNG Plant Module	300,000 bpcd Gasoline Refinery (Reference)
Particulates, lb/hr	20	353
Sulfur Dioxide (SO_2), lb/hr	8	1918
Hydrocarbons (HC), lb/hr	677	6418
Carbon Monoxide (CO), lb/hr	12	138
Nitrogen Oxides (NO_x), lb/hr	217	1846

must also hold for the present case. Summaries of Federal and state ambient air quality standards and predicted maximum concentrations for the 300,000 bpcd refinery "reference" module shown on Tables 6.1-5, 6, and 7 are applicable in this comparison.

The trend of the scheme is towards the "worst" and most conservative estimate, i.e. Scheme 3. As seen in these tables, the computed maximum concentrations of the refinery "reference" module, which has much higher air emissions than the SNG plant, are below the Federal ambient air quality standards for particulates, SO_2, NO_x, and CO that will be released by a 125 MM scfd SNG plant. No attempt has been made to characterize hydrocarbon emissions.

The SNG plant HC emission given in Table 6.2-1 is smaller than that of the refinery "reference" module by a factor of 9. Therefore, if all the conditions explained in the previous discussions hold, and if a decrease of HC emission by a factor of 9 would reduce the computed maximum concentration of the pollutant by the same factor, then the results for the three schemes would be those given in Table 6.2-2. The computed short-term HC maximum concentration for typical meteorological conditions would be below the EPA 3-hour non-methane hydrocarbon guideline. The computed short term HC maximum concentrations for unstable and stable meteorological conditions exceed the EPA guideline.

Water Quality Impact

SNG plant modules based on naphtha feed have minimal liquid effluents. M. W. Kellogg's report for EPA on a 150 MM scfd SNG plant (KE-129), addresses the sources of liquid effluents, viz., cooling tower blowdown, boiler blowdown, and backwash water from water treating process. Liquid effluents of this type consist mainly of totally dissolved solids (TDS)

TABLE 6.2-2
3-HOUR NON-METHANE HYDROCARBONS
(UNITS ARE ug/m^3 WITH ppm IN PARENTHESES)

	Scheme 1	Scheme 2	Scheme 3
EPA Guideline	160(0.24)	160(0.24)	160(0.24)
Computed Short-Term Maximum[++] Unstable Condition	167(0.25)	208(0.32)	250(0.38)
Computed Short-Term Maximum[++] Stable Condition	4444(6.70)	5556(8.37)	6667(10.04)
Computed Short-Term Maximum[++] Typical Conditions	67(0.10)	84(0.13)	101(0.15)

[++] Maximum values are those that occur on or outside the plant boundary.

of about 37,000 ppm. The boiler blowdown, cooling tower blowdown, and backwash water from water treating process contributed 4%, 5%, and 91% of the TDS, respectively.

EPA has placed no restriction on total dissolved solids in its effluent limitation guidelines and new source performance standards. Therefore liquid effluents from an SNG plant cannot be categorized as pollutants.

Raw Material Availability

Raw material pertains to both feedstock and water. Their implications for the current study are presented separately.

Feedstock Availability

Naphtha is the basic feedstock being considered for the SNG plants. Other feedstocks such as ethane, LPG, middle distillates, gas oil, and crude oil can be used by SNG plants, but their availability under the FEA's mandatory oil-allocation program (FE-085) is not certain.

Naphtha is chiefly a domestic product and can be transported via product pipelines, waterways, or railroads. Typically a 125 MM scfd SNG plant will need about 25,000 barrels of naphtha per day (LI-095). Thus, it is rather important for a proposed SNG plant of this capacity to be sited along the feedstock routes. As mentioned in the previous section, the existing waterways and railroad facilities can be used for the transportation of naphtha. Movements of naphtha through both modes of transportation generally belong to the private sector with little Federal regulation other than for safety and environmental reasons. The main environmental concern with these modes of transportation, especially tank barges through waterways is the potential hazard of naphtha spills.

Proposed SNG plants may require new feedstock pipeline routes. The ownership and operation of the oil product pipeline system is generally private and has little Federal regulation other than for safety and environmental reasons. New pipeline routes will create some environmental effects during the phase of construction, but these effects are beyond the scope of the present work and are not dealt with here. The major concern with the operation of a pipeline system is the potential hazard of spill. In the event of spill, some naphtha could possibly reach water bodies in the form of non-degradable organics as discussed in Section 6.1.2.1. Therefore, in siting SNG plants, potential environmental effects of feedstock pipeline construction and operation must be given due consideration.

Water Availability

SNG plants' makeup water requirements will be about 4.9 gallons per thousand scf of SNG produced (WO-046). A typical 125 MM scfd SNG plant will need as much as 612,500 gallons of water per day. This amount of water may or may not be critical to SNG plant siting. Constraints on water availability are discussed in Section 6.1.2.2.

6.3 LNG Plant Impact

Liquefied natural gas (LNG) is one of the most promising sources of supplemental energy. The usual LNG "life-cycle" embraces: natural gas supply and delivery, liquefaction and storage, then shipping, followed by receiving storage and regasification. Peak shaving is the predominant LNG application in the U.S. Peak shaving consists chiefly of gas delivery, liquefaction and storage, and regasification. This operation is described in Section 2.2. Development of the large Alaskan natural gas reserve could lead to a domestic base load LNG industry.

Major areas under consideration are effluents, raw material (feedstock and water) availability, and product transportation which might create constraints on the siting of an LNG plant. To provide a perspective on LNG technology, two types of plants are considered: one with 10 MM scfd liquefaction capacity and a 100 MM scfd regasification rate for peak shaving, the other a 750 MM scfd plant for base load purposes.

6.3.1 LNG Plant Effluents

Liquefaction and regasification plants are the main sources of effluents. Their effects on siting are addressed in this section.

6.3.1.1 Liquefaction Plant

Potential primary effluent sources found within the liquefaction plant include air emissions from boiler stacks and miscellaneous fugitive losses, and liquid effluents from water treatment facilities.

Air Emissions Impact

Potential air emissions from a peak shaving plant module and a 750 MM scfd base load LNG liquefaction plant are described in Section 3.3 and are summarized in Table 6.3-1. The air emissions from a 300,000 bpcd gasoline refinery, which serves as a reference for ambient air quality analysis, are also included. Observe in the table that the estimated particulates, sulfur dioxide, NO_x, and carbon monoxide emissions from both 10 MM scfd and 750 MM scfd LNG liquefaction plants are less than or of the same order as the calculated air emissions of the refinery "reference" module. These observations, along with the results of the air emissions impact of a 300,000 bpcd "reference" module in Section 6.1.1.1, indicate that both peak shaving and base load plants will have minimal impact on the ambient air quality with regard to these potential pollutants. With regard to hydrocarbon pollution, the LNG hydrocarbon emissions are primarily methane, and are not regulated within the non-methane hydrocarbon guideline.

Water Quality Impact

The major liquid effluent streams of LNG liquefaction plants include acid and caustic wash water streams used for demineralizer regeneration. The LNG liquefaction plant described in Section 3.3 includes a holding pond for the effluent streams. This method is a common practice in the process and utility industries. Discharging liquid effluents into a holding pond within the property of the liquefaction plant is not considered a menace to the environment. Of course, this assumes that the liquid effluents will be in an immobile condition, i.e., there will be no seepage into the groundwater bodies. To achieve this condition, proper siting is required. The hydraulic and geological

TABLE 6.3-1

AIR EMISSIONS - LNG MODULE COMPARISONS

Pollutant	10 MM scfd LNG Plant Module	750 MM scfd LNG Plant Case Study	300,000 bpcd Gasoline Refinery (Reference)
Particulates, lb/hr	2	73	353
Sulfur Dioxide (SO_2), lb/hr.	<1	2,410	1,918
Hydrocarbons (HC), lb/hr.	20	1,330	6,418
Carbon Monoxide (CO), lb/hr.	2	80	138
Nitrogen Oxides (NO_x), lb/hr.	30	2,570	1,846

conditions of a selected site must be known to allow prediction of its potential to hold the discharged liquid effluents.

6.3.1.2 Regasification Plant

Potential emission sources found within the regasification plant include possible "negative" thermal discharge of circulating water.

A potential environmental issue that will stem from the process operation of the regasification plant is the so-called "negative" thermal pollution. It results from the use of water for vaporizing and warming the gas. In the process the discharge water will be several degrees colder than the incoming natural water stream. Existing water-quality standards for temperature generally specify limits as the temperature rises above some specified level, ranging from 0° to $5^{\circ}F$. However, some state jurisdictions set standards for both positive and negative temperature changes. Although "negative" thermal discharge is beyond the scope of this study, it is mentioned as a unique form of pollution that could pose a siting problem for a regasification plant using a once-through heating system.

6.3.2 Raw Material Availability

There are some environmental impacts and problems in siting of an LNG plant that are associated with raw material availability. Raw material in the discussions refers to both feedstock and water.

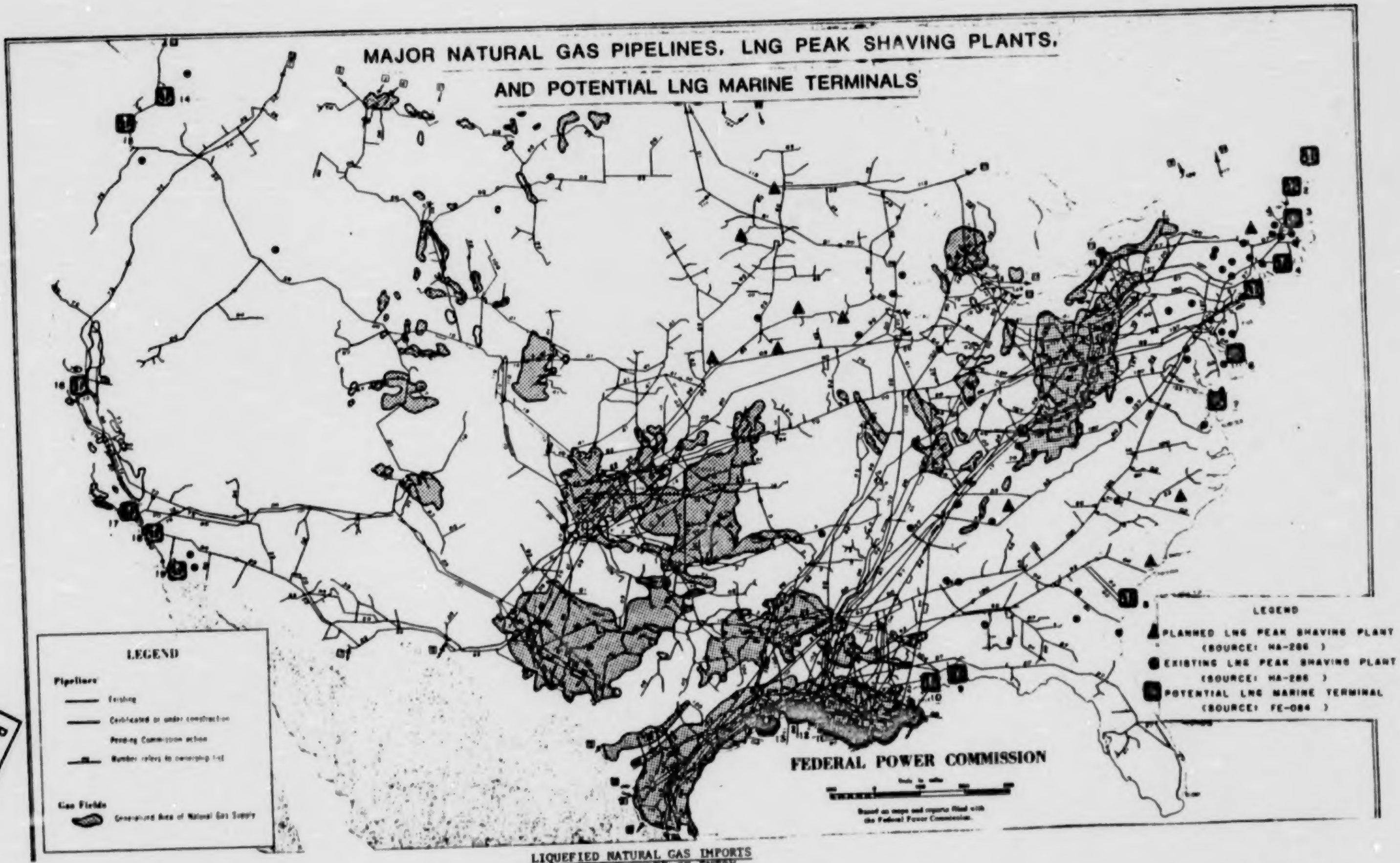
6.3.2.1 Feedstock Availability

Natural gas is the feedstock for an LNG liquefaction plant. It is transported by gas pipeline. An LNG peak shaving plant must be sited along the main arteries of the natural gas pipeline network. The main air emissions will come from the compressor stations. Compressor stations can be driven by gas engines, gas turbines, or by electricity. Emissions from the first two prime movers are predominantly NO_x. Since the frequency of compressor stations is one every 50 to 75 miles (BA-234), the NO_x emissions are unlikely to have a significant adverse effect on the environment. Electrically driven compressor stations must be energized through an electrical system, thus siting must consider this factor. Major U.S. gas pipelines and ports of entry for LNG are shown in Figure 6.3-1.

6.3.2.2 Water Availability

A major factor that needs to be considered in siting an LNG liquefaction plant is water availability. Cooling water usage for a 750 MM scfd LNG liquefaction plant may range from 500 to 1,000 million gallons per day (FE-084). Furthermore, total steam power for a 750 MM scfd LNG liquefaction plant will add to the fresh water make-up requirement (FE-084). The water flow rate for a regasification plant that will regasify 750 MM scfd of LNG may range from 300 to 500 million gallons per day. The water requirements for 10 MM scfd peak shaving plants will be much less.

The need for such substantial quantities of water will present a siting problem at some U.S. sites.


MAJOR NATURAL GAS PIPELINES, LNG PEAK SHAVING PLANTS,
AND POTENTIAL LNG MARINE TERMINALS
LEGEND
Pipelines
Existing
Certificated or under construction
Pending Commission action
Number refers to ownership list
Gas Fields
Generalized Area of Natural Gas Supply
LEGEND
▲ PLANNED LNG PEAK SHAVING PLANT (SOURCE: MA-286)
● EXISTING LNG PEAK SHAVING PLANT (SOURCE: MA-286)
■ POTENTIAL LNG MARINE TERMINAL (SOURCE: FE-084)
FEDERAL POWER COMMISSION

LIQUEFIED NATURAL GAS IMPORTS
POSSIBLE PORTS OF ENTRY

	AREA	WATER DEPTH (feet)	TIDE RANGE (feet)	REMARKS
1.	Penobscot Bay, Maine	40	9.7	Substantial distance from major gas transmission lines.
2.	Portland, Maine	40	9.0	Substantial distance from major gas transmission lines.
3.	Boston, Massachusetts	40	9.5	Densley populated.
4.	Conanicut Island, Rhode Island	40	3.2	Good location for receiving LNG. Low demand area.
5.	New York, New York	35-37	5.0	High marine traffic density. Densely populated.
6.	Delaware River	40	6.0	Several possible sites. High demand area - Near major gas transmission lines.
7.	Chesapeake Bay, Virginia	45	3.0	Several possible sites. Heavy Navy traffic.
8.	Savannah, Georgia	40	7.0	Near major gas transmission line.
9.	Mobile, Alabama	40	6.0	Near major gas transmission lines.
10.	New Orleans, Louisiana	40	3.0	Near major gas transmission lines.
11.	Lake Charles, Louisiana	40	2.0	Near major gas transmission lines.
12.	Sabine, Texas	40	6.0	Near major gas transmission lines.
13.	Galveston-Houston, Texas	40	6.0	Near major gas transmission lines.
14.	Tacoma, Washington	45	6.8-11.8	Good location for receiving LGN. Near major gas transmission line.
15.	Portland, Oregon	35-40	2.4	Near major gas transmission line.
16.	San Francisco - Oakland, Calif.	40	3.2-6.0	High demand area - Near major gas transmission line.
17.	Hueneme, California	40	2.8-5.4	Near major gas transmission line. 120,000 cubic meter ships.
18.	Los Angeles - Long Beach	40-50	2.8-5.4	High demand area - Near major gas transmission line.
19.	San Diego, California	40	3.0-5.7	Near major gas transmission line. Heavy Navy traffic.

FIGURE 6.3-1. LNG PIPELINES, PLANTS, AND POTENTIAL ENTRY PORTS

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6.3.3 Product Shipping and Receiving

Since LNG is predominantly transported by ship, product shipping and receiving must be given some considerations when siting LNG plants. During in-port operations, loading and unloading of LNG will result in some atmospheric emissions, primarily from boil-off of gas and from the use of other fuels. Considerable quantities of boil-off gas have been observed at the site during and after LNG unloading. There are also some water effluents, as well as solid wastes, resulting from the disposal of shipboard debris and sanitary wastes.

The foremost concern during product shipping and receiving operations is human safety. Spillage of LNG, because of its cryogenic temperatures, can cause brittle fracture. Also spillage is a potential hazard, arising from the LNG fuel properties. Methane-air mixtures are flammable in the concentration range from 5.3 to 13.9 volume percent methane (WA-157). Other environmental effects that may arise from product shipping and receiving operations are given in Table 6.3-2.

Another siting consideration is the fact that current U.S. ports are not capable of handling the new generation of LNG ships. Potential LNG marine terminals are shown in Figure 6.3-1. The development of these terminals will have some secondary environmental effects. LNG shipping, receiving, and storage, must abide by the National, State, and Local LNG Codes and Standards. An excerpt of the current status of these LNG codes and standards appears in reference BA-276.

TABLE 6.3-2

APPROXIMATE GUIDE TO APPRAISING ENVIRONMENTAL FACTORS OF LNG FACILITIES

(Source: WA-157)

0 – NONE 1 – SOME 2 – MAJOR	EFFLUENTS						IMPACTS				
	THERMAL	CHEMICAL			NOISE	HYDRAULIC	ECOLOGICAL		HUMAN HEALTH	HUMAN SAFETY	HUMAN ACTIVITIES
		AIRBORNE	LIQUID	SOLID			TERREST.	AQUATIC			
I. LIQUEFACTION PLANT											
A. GAS CLEAN–UP	0	2	1	1	0	0	0	1	1	0	1
B. COMPRESSION	1	0	0	0	2	0	0	0	1	1	1
C. COOLING	2	0	1	1	0	1	1	2	1	0	1
D. STORAGE	0	1	0	0	0	0	1	0	0	2	1
E. AUXILIARIES	2	2	1	0	1	0	1	1	1	0	0
II. MARINE TRANSP.											
A. LIQUID LOADING	0	1	1	0	0	0	1	1	1	2	1
B. DEEP WATER OP.	0	2	1	1	0	0	0	1	0	1	1
C. IN–PORT OPER.	1	2	1	1	1	2	0	2	1	1	2
D. LIQUID UNLOAD	0	1	1	0	0	0	1	1	1	2	1
III. RECEIVING TERM.											
A. TRANSFER	0	2	0	0	1	1	1	1	0	1	1
B. STORAGE	0	1	0	0	0	0	1	0	0	2	1
C. REGASIF.	2	1	1	0	0	0	0	1	1	1	0
D. ODORIZATION	0	2	0	0	0	0	0	0	2	0	1
E. AUXILIARIES	0	1	1	0	0	0	0	0	1	0	1
IV. LAND TRANSP.											
A. LOAD/UNLOAD	0	1	0	0	0	0	1	1	1	2	0
B. TRANSPORT	0	2	0	0	2	0	2	2	0	2	2
C. MAINT.	0	0	1	1	1	0	0	1	0	1	0
V. PEAK SHAVING											
A. GAS CLEAN–UP	0	1	0	1	0	0	0	0	1	0	1
B. COMPRESSION	1	0	0	0	2	0	0	0	1	1	1
C. COOLING	2	0	1	0	0	1	1	2	1	0	1
D. STORAGE	0	1	0	0	0	0	1	0	0	2	1
E. REGASIF.	2	1	1	0	0	0	0	1	1	1	0
F. ODORIZATION	0	2	0	0	0	0	0	0	2	0	1

0 - Suggests that there may be no need to evaluate or assess.

1 - Indicates that the effluent or impact may have to be considered but detailed evaluation or assessment is probably unnecessary.

2 - Indicates that the effluents and impacts which will probably deserve quantitative evaluation and assessment.

APPENDIX 6.1-1

PRIMARY (SECONDARY) AMBIENT AIR QUALITY STANDARDS OF ARBITRARILY SELECTED STATES

PRIMARY (SECONDARY)

AMBIENT AIR QUALITY STANDARDS OF ARBITRARILY SELECTED STATES

(Units are micrograms per cubic meter with ppm in brackets)

Pollutant	California	Colorado	Delaware	Florida
Sulfur Oxides	See Following Pages			
Annual Averages (A.M.)[1]		25	80(60)	60
24-hr. Maximum[3]		150	370(260)	260
3-hr. Maximum[3]			(1,300)	1,300
30-minute Maximum				
Particulate				
Annual Average (G.M.)[2]		55	70(60)	60
24-hr. Maximum[3]		180	200(150)	150
5-hr. Maximum				
3-hr. Maximum				
1 hr. Maximum			500	
Nitrogen Dioxide				
Annual Average (A.M.)			100(100)	100
Non-Methane Hydrocarbons				
3-hr. Maximum[3] (6-9 A.M.)			131(131)	160
Carbon Monoxide				
8-hr. Maximum[3]			9,200(9,200)	10,000
1-hr. Maximum[3]			40,000(40,000)	40,000

---

1. Arithmatic mean.

2. Geometric mean.

3. Not to be exceeded more than once per year.

CALIFORNIA: SAN FRANCISCO

Bay Area Air Pollution Control District Regulations Applicable to Refineries

1. No person shall cause, let, permit, suffer, or allow the emission for more than three minutes in any one hour of a gas stream containing air contaminants which, at the emission point or within a reasonable distance of the emission point, in as dark or darker in shade as that designated as No. 1 on the Ringleman Chart as published in the United States Bureau of Mines Information Circular 7718, or of such capacity as to obscure an observer's view to a degree equal to or greater than does smoke described above.

2. The emission does not contain more than "n" grains of particulate matter for standard cubic feet, where

$$n = 0.06/L$$

   and L is the significant dimension of the emission point in feet.

3. No person shall cause, let, permit, suffer, or allow any emission from a heat transfer operation of particulate matter in excess of 0.15 grain per standard dry cubic foot of exhaust gas.

California: San Francisco (cont.)

Bay Area Air Pollution Control District Regulations Applicable to Refineries

4. No person shall cause, let, permit, suffer, or allow any emission of SO_2 which results in ground level concentrations of SO_2 at any given point in excess of 1.5 ppm (Vol) for 3 consecutive minutes or 0.5 ppm (Vol) averaged over 60 consecutive minutes, or 0.04 ppm (Vol) averaged over 24 hours, or any of the following limits:

SO_2 Concentration ppm (Vol)	Total Cumulative Exposure Between Midnight and the Next Succeeding Midnight in Hours
1.5	0.05
0.5	1.0
0.3	3.2
0.1	9.6
0.04	24.0

5. No person shall cause, let, permit, suffer, or allow the emissions of gas containing SO_2 in excess of 300 ppm (Vol).

6. No person shall cause, let, permit, suffer, or allow an emission of an effluent containing a concentration of more than 50 ppm of organic compounds calculated as hexane (or 300 ppm total "carbon").

PRIMARY (SECONDARY)

AMBIENT AIR QUALITY STANDARDS OF ARBITRARILY SELECTED STATES

(Units are micrograms per cubic meter with ppm in brackets)

Pollutants	Georgia	Illinois	Indiana	New Mexico
Sulfur Oxides				
Annual Averages (A.M.)[1]	43		80(60)	[0.02]
24-hr. Maximum[3]	229		365(260)	[0.10]
3 hr. Maximum[3]				
Particulate				
Annual Average (G.M.)[2]	60	75(60)	75(60)	60
24-hr. Maximum[3]	150	260(150)	260(150)	150
5-hr. Maximum				
3-hr. Maximum				
1-hr. Maximum				
Nitrogen Dioxide				
Annual Average (A.M.)	100	100	100	[0.05]
Non-Methane Hydrocarbons				
3-hr. Maximum[3] (6-9 A.M.)	98	160	160	[0.19]
Carbon Monoxide				
8-hr. Maximum[3]	10,400	10,000	10,000	[8.7]
1-hr. Maximum[3]	40,000	40,000	40,000	[13.1]

---

[1] Arithmatic mean.

[2] Geometric mean.

[3] Not to be exceeded more than once per year.

PRIMARY (SECONDARY)

AMBIENT AIR QUALITY STANDARDS OF ARBITRARILY SELECTED STATES

(Units are micrograms per cubic meter with ppm in brackets)

Pollutants	Maryland	Massachusetts	Montana	New Jersey	New Mexico
Sulfur Oxides					
Annual Averages (A.M.)[1]	79(39)	73	[0.02]	80(60)	[0.02]
24-hr. Maximum[3]	262(131)	300	[0.10]	365(260)	[0.10]
3-hr. Maximum[3]				(1,300)	
30-minute Maximum					
Particulate					
Annual Average (G.M.)[2]	75(65)	75	75	75(60)	60
24-hr. Maximum[3]	160(140)	180	200	260(150)	150
5-hr. Maximum					
3-hr. Maximum					
1-hr. Maximum					
Nitrogen Dioxide					
Annual Average (A.M.)	100			100	[0.05]
Non-Methane Hydrocarbons					
3-hr. Maximum (6-9 A. M.)		120		160	[0.19]
Carbon Monoxide					
8-hr. Maximum[3]		9,200		10,000	[8.7]
1-hr. Maximum[3]				40,000	[13.1]

---

1. Arithmatic mean.
2. Geometric mean.
3. Not to be exceeded more than once per year.

PRIMARY (SECONDARY)

AMBIENT AIR QUALITY STANDARDS OF ARBITRARILY SELECTED STATES

(Units are micrograms per cubic meter with ppm in brackets)

Pollutant	New York	North Carolina	North Dakota
Sulfur Oxides			
Annual Averages (A.M.)[1]	80	60	60
24-hr. Maximum[3]	365 (260)	260	260
3-hr. Maximum[3]		1,300	
30-minute Maximum			
Particulate			
Annual Average (G.M.)[2]		60	60
24-hr. Maximum[3]	250	150	150
5-hr. Maximum			
3-hr. Maximum			
1-hr. Maximum			
Nitrogen Dioxide			
Annual Average (A.M.)	100	100	100
Non-Methane Hydrocarbons			
3-hr. Maximum[3] (6-9 A.M.)	160	160	160
Carbon Monoxide			
8-hr. Maximum[3]	10,000	10,000	10,000
1-hr. Maximum[3]	40,000	40,000	40,000

---

[1] Arithmatic mean.

[2] Geometric mean.

[3] Not to be exceeded more than once per year.

PRIMARY (SECONDARY)

AMBIENT AIR QUALITY STANDARDS OF ARBITRARILY SELECTED STATES

(Units are micrograms per cubic meter with ppm in brackets)

Pollutant	Texas	Utah	Virginia	Wyoming
Sulfur Oxides	See Tables 6.1-5, -6, and -7			
Annual Averages (A.M.)[1]		[0.03] ([0.02])	80	60
24-hr. Maximum [3]		[0.14] ([0.10])	365	260
3-hr. Maximum [3]			1,300	1,300
30-minute Maximum				
Particulate				
Annual Average (G.M.)[2]		90	75(60)	60
24-hr. Maximum[3]			260(150)	150
5-hr. Maximum				
3-hr. Maximum				
1-hr. Maximum				
Nitrogen Dioxide				
Annual Average (A.M.)		[0.05]	100	100
Non-Methane Hydrocarbons				
3-hr. Maximum [3] (6-9 A.M.)		[0.24]	160	160
Carbon Monoxide				
8-hr. Maximum [3]		[9]	10,000	10,000
1-hr. Maximum [3]		[35]	40,000	40,000

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1. Arithmatic mean.
2. Geometric mean.
3. Not to be exceeded more than once per year.

APPENDIX 6.1-2

WATER QUALITY MODELS

Mathematical models are useful tools in computing the pollutant concentrations in receiving waters which result from predicted refinery effluent discharges. Two levels of complexity are exhibited by the models. A very simple model gives background concentrations some distance from the effluent outfall and applies to well mixed streams. The other model, in addition to giving background concentrations, computes constant concentration contours extending from effluent outfall to the region of background concentrations. This model, referred to as the Water Quality Display Model (WQDM), is especially useful in showing pollutant distributions in tidal waters during conditions of flood, slack, and ebb tides. The two types of models will be discussed separately.

(a) Well Mixed Stream Model

In either a fast flowing stream or in a tidal waterway, pollutants introduced into the main flow channel are rapidly well mixed with the receiving waters by turbulent mixing. This means that at some relatively short distance from effluent outfall, a background concentration of the effluents in the receiving waters will exist. Higher concentrations naturally occur at outfall, but they decrease to the background level over a distance required for the well mixed condition to prevail. The steady-state or mean background level is determined by the combination of the effluent concentration of pollutants, the effluent flow rate, and the net outflow of the stream or waterway.

The number which is of interest in determining the water quality impact of the effluent is the mean number of parts per million (or mg/ℓ) of a particular pollutant which exists in the receiving waters which would not have been there had the refinery effluent not been discharged. For well mixed pollutants this number is easily obtained from the formula:

$$\left\{\begin{matrix}\text{Mean Additional}\\ \text{Pollutant Concentration}\end{matrix}\right\} = \left\{\text{Dilution Factor}\right\} \times \left\{\begin{matrix}\text{Effluent Pollutant}\\ \text{Concentration}\end{matrix}\right\}$$

where the dilution factor is simply the ratio of the effluent volumetric flow rate to the sum of the net stream outflow rate and the effluent volumetric flow rate.

When this model is applied to a fast flowing, non-tidal stream, the concentration gradients near outfall mentioned previously are essentially constant and generally tend to extend downstream only. When this simple model is applied to tidal waters, however, it should be recognized that tidal flows will cause temporal variations of concentrations in the vicinity of effluent outfall during each day which extend both up and downstream. Also, as mentioned above, concentrations near outfall will naturally exceed the mean concentrations computed above. Ebb tide concentrations in the vicinity of effluent outfall will be less than flood tide concentrations there because of greater ebb currents. Slack water outfall concentrations will be substantially greater than either ebb or flood tide concentrations. Slack water conditions fortunately exist for relatively short periods, however. Gradients in concentrations of varying magnitude exist at all times between initial effluent concentrations at outfall and the mean concentrations computed according to the simple model described above. The mean levels will exist at some distance from outfall, however, and they are perhaps the best measure of the impact on area water quality of additional waste water discharges.

It should be noted that the mean additional pollutant concentration computed by the model assumes the effluent is introduced into pure ambient water. When a pollutant concentration, x, preexists in the receiving waters, the total resultant concentration in the waters is given by:

$$\left\{\begin{matrix}\text{Total Pollutant}\\ \text{Concentration}\end{matrix}\right\} = x + \left\{\text{Dilution Factor}\right\} \left\{\begin{matrix}\text{Effluent Pollutant}\\ \text{Concentration}\end{matrix} - x\right\}$$

This equation follows from conservation of mass when two volumes of fluid are added together. It should also be noted that the mean, steady-state levels computed by the model depend on net stream outflow, whereas the localized concentration gradients near outfall discussed above for tidal waters depend temporally on tidal flows.

(b) Water Quality Display Model (WQDM)

To quantify the distribution of pollutants near effluent outfall which the simple model described above does not do, the WQDM can be used. This model predicts relative pollutant concentrations in the vicinity of outfall, and its outputs can be scaled to predict absolute pollution levels from outfall to the region of background levels. Discussions of both the WQDM and how its results are scaled are presented in this section.

The WQDM is a computer model which computes stream functions and diffusion equation solutions. From these results the streamlines of flow in a stream can be plotted, and contours of constant pollutant concentration surrounding effluent outfall can also be plotted. The model utilizes Monte Carlo techniques to obtain its numerical results.

Application of the WQDM to the water quality problem under consideration here involves two main assumptions. The first is that flow in the waterways investigated can be described substantially correctly by potential flow. This means that the stream function, $\Phi(x,y)$, from which the water velocity field can be constructed can be obtained as the solution of Laplace's equation, $\nabla^2 \Phi(x,y) = 0$. Also, the problem is assumed to be two dimensional. Except for small regions near certain boundaries of minor importance to the overall results, potential flow is a valid assumption for the streams studied. Also, the depth dimension of the waterways is used in the construction of boundary conditions for each problem so that two dimensional solutions are essentially valid. The second assumption is that periods of steady-state flow exist, corresponding to ebb, flood, and slack tide conditions, for time intervals long enough for roughly steady-state concentrations to be established. This is valid for roughly two hour periods spanning peak ebb flows, peak flood flows, and slack water conditions.

The basis of obtaining Monte Carlo solutions to Laplace's equation and to the diffusion equation stems from the similarity of the equations obeyed by a particle performing a random walk and the finite difference equations corresponding to Laplace's equation and the diffusion equation. Brown discusses the application of Monte Carlo techniques to these two equations (BR-132).

Application of the WQDM to a problem involves the following steps. First, the stream geometry is gridded and boundary values are assigned to each point on the closed boundaries of the stream. The stream shores comprise two boundaries and cuts across the stream both up and downstream from the region near outfall are used to close the boundaries. Since each shore is assumed to be a limiting streamline, arbitrary boundary values can be assigned to each. Usually one shore is set to zero and the other is set at unity. Boundary values along the cross-stream cuts are set to monotonically increasing values from zero to one. The exact variation along these segments of the boundaries is tied to the channel depth along each cut. The values reflect more flow at deeper parts of the channel. For the thusly established conditions, the Monte Carlo solution of Laplace's equation is obtained. Unlike finite difference techniques, the Monte Carlo approach can be used to find the solution at a single point within the modeled region. With the stream function, Φ (x,y), computed for all points in the modeled region, the streamlines of the flow can be obtained as lines of constant Φ (x,y).

Next, solutions of the diffusion equation must be obtained. To do this the results of the stream function computations must be available as is explained as follows. The basic operation in the Monte Carlo models is the random movement of a particle from one grid point to another. For a particle at an arbitrary internal grid point, it may move up, down, left, or right. In solving Laplace's equation, the probabilities associated with moving in each direction are equal. But solution of the diffusion equation in the presence of advective flow requires that movement with the current be favored. It is, therefore, necessary to know the velocity field at each point of the stream so that the probabilities governing the random walk can be properly adjusted at each point in the stream. Since the velocity at any point is proportional to the gradient of the stream function, the stream function previously computed can be used to set up the four required probabilities as given by:

$$p_{x+} = \tfrac{1}{4}\left[1 + \frac{u_x}{\delta r}\right]$$

$$p_{x-} = \tfrac{1}{4}\left[1 - \frac{u_x}{\delta r}\right]$$

$$p_{y+} = \tfrac{1}{4}\left[1 + \frac{u_y}{\delta r}\right]$$

$$p_{y-} = \tfrac{1}{4}\left[1 - \frac{u_y}{\delta r}\right]$$

where $r = \frac{2K}{\delta^2}\left[1 + \left(1 + \frac{\delta^2 c^2}{4K^2}\right)^{\frac{1}{2}}\right]$

$c^2 = u_x^{\,2} + u_y^{\,2}$

δ = a scale factor,(ft/grid division),

K = the dispersion coefficient, (ft^2/min)

$u_x = \beta\ (\Delta\Phi)_y$

$u_y = \beta\ (\Delta\Phi)_x$

β = a proportionality constant; positive for downstream flow and negative for upstream flow, and

$(\Delta\Phi)_y$ and $(\Delta\Phi)_x$ = the derivatives of $\Phi(x,y)$ in the y and x directions, respectively.

With the stream function input, the WQDM computes relative pollutant concentrations at each point in the modeled region by simulating the turbulent dispersion of pollutants entrained in advective flow for roughly two hours. From these results contours of constant concentration surrounding outfall can be drawn. Peak or 100% concentration is at outfall. The region beyond the zero percent concentration contour corresponds to the mean background level region.

Scaling the contours to absolute levels is done individually for each pollutant as follows. The zero percent contour level is computed by the well mixed stream model. The net stream outflow is used to compute the dilution factor for this case. The 100% contour for ebb and flood flows is also computed by the model of Section (a); however, calculation of the dilution factor is modified for these cases. In defining the dilution factor for these cases, it is important to define the significance of the 100% contour. Pollutant concentrations precisely at effluent outfall are not immediately diluted, therefore, the raw effluent pollutant concentration could be taken to correspond to the 100% contour. This was not done, however. Instead, it was deemed reasonable to associate the 100% contour concentration with the mean concentration occurring over the smallest resolvable region of the modeled area. This region is defined by a square with sides the length of a single grid division. For this interpretation of the 100% contour, it follows that the dilution factor is computed as before, except the stream flow is taken to be only the amount that flows through the unit square centered at effluent outfall. Also, it is part of either ebb or flood flows that are used in the calculation, not net stream outflow.

Computation of the 100% concentration for slack water is based on the same interpretation of the 100% contour as above; however, the absence of stream flow means that a dilution factor cannot be used. Instead, the mean concentration over the minimum square is computed assuming diffusion from the center of the square for a two hour period. The concentration for such a problem has a Gaussian distribution from the center of the square, and its sigma is a function of time. The sigma at two hours can be compared to the dimensions of the minimum square to allow scaling the minimum square in terms of the Gaussian form of the pollutant concentration. It is then easy to compute a scale factor for the raw effluent pollutant concentration which gives the mean concentration over the area of the minimum square. This factor is simply the average of a Gaussian density over the scaled dimensions of the minimum square.

As for the simple model of Section (a), the concentrations discussed above are for discharges into pure water. Total background concentrations resulting from discharges into preexisting pollutants are computed as discussed in Section (a).

APPENDIX 6.1-3

MAJOR WATER LAWS

Law of River Compacts

These compacts are generally made within a river basin agency and have a direct effect on the member states of that agency.

The compacts exist to mediate the problems associated with allocation of interstate water and the administration of water rights. Because of these problems and existing or impending litigation, several affected States have entered into interstate compacts or requested court apportionment of the affected waters for the river systems.

The Federal Constitution provides that no State shall enter into any agreement or compact with another State, or with a foreign power, without the consent of Congress. Approval by Congress is required once the compact is ratified by the several States and usually provides for a Federal representative serving and reporting on the negotiations.

Upper Missouri River Basin

The interstate compacts which are applicable to the Fort Union region are the Belle Fourche River Compact and Yellowstone River Compact.

"The Belle Fourche River Compact between Wyoming and South Dakota was approved by the Act of February 26, 1944. Under this compact water right priorities theretofore established in one State were to be recognized in the other. Of the remaining unappropriated water, 90 percent is to be allocated to South Dakota and 10 percent to Wyoming. Diversions and impoundments of water in one State for use in the other State are authorized where State appropriation laws are observed.

The Yellowstone River Compact among Wyoming, Montana, and North Dakota was approved by the Act of October 30, 1951. It divides Yellowstone River Basin Surplus waters (1) in the Clarks Fork, 60 percent to Wyoming and 40 percent to Montana;

(2) in the Big Horn River, 80 percent to Wyoming and 20 percent to Montana; (3) in the Tongue River, 40 percent to Wyoming and 60 percent to Montana; and (4) in the Powder River, 42 percent to Wyoming and 58 percent to Montana. The Compact provides that the three signature States will not singly or jointly take actions which adversely affect Indian water rights to those waters of the Yellowstone River or its tributaries. Diversions and impoundments in one State for use in another State are authorized where State appropriation laws are observed. Diversions out of the Yellowstone Basin require the unanimous consent of all of the compacting States" (NO-055).

Upper and Lower Colorado River Basins

"The Colorado River is perhaps the most regulated river in the United States, and its utilization is such that very little usable water now discharges from its mouth into the Gulf of California. The cornerstone is the Colorado River Compact of 1922, which the seven Basin states negotiated pursuant to the Act of August 19, 1921 (42 Stat. 171). This Compact divides the Colorado River Basin into two parts; i.e., the Upper Basin and the Lower Basin, separated at a point on the river near the Utah/Arizona border known as Lee Ferry. Article III(a) apportions to each basin in perpetuity 7.5 m.a.f. of water per year. Article III(c) provides that any future Mexican water rights, recognized by the United States, are to be supplied as provided in the Compact. Article III(d) obligates the Upper Basin not to deplete the flow at Lee Ferry below an aggregate of 75 m.a.f. for any period of 10 consecutive years reckoned in continuing progressive series. In 1948 the Upper Basin States entered into a compact to divide the water of the Upper Basin as described in Article III(a) apportions among the States of Arizona, Colorado, New Mexico, Utah, and Wyoming the Colorado River Compact water in the following manner:

(1) Arizona, 50,000 a.f.

(2) Colorado, New Mexico, Utah, and Wyoming, after deduction of Arizona's 50,000 acre-feet: Colorado, 51.75 percent, New Mexico, 11.25 percent, Utah, 23 percent, and Wyoming, 14 percent.

Article III(b)3 provides that no state shall exceed its apportioned use in any year when such use deprives another state of its water during that year. Curtailment in use of water apportioned is to be determined by the Commission. The Commission is to determine and allocate losses of water as a result of reservoir storage. The Upper Colorado River Commission is created as an interstate administrative agency and its duties are defined by Article VIII of the Compact. The Compact is not to interfere with the right or power of any state to regulate within its boundaries the appropriation, use, and control of water apportioned to such state. The failure of any state to use water shall not constitute a relinquishment or a forfeiture of the right to use that water. Article XIX provides that the obligation of the United States to the Indian tribes, the Mexican Treaty or any rights of the United States to acquire waters in the Upper Colorado River System are not to be affected" (US-168).

State Water Laws

In all parts of the country, water laws are largely based on the Riparian Doctrine, the Appropriation Doctrine, or a combination of both. A riparian right to withdraw water is based on the ownership of land next to a surface-water body. The right is independent of the use or non-use of the water. An appropriation right is based upon the beneficial use of the water. In other words, the first to appropriate and use the water has a priority over others who come along and appropriate at a later time. An appropriation right is independent of the location of the land with respect to the water.

Figure B-1 shows that all states roughly east of the 95th meridian follow the Riparian Doctrine exclusively, with the exception of Mississippi and Florida. This eastern half of the country coincides with the area of water surplus shown on Figure 6.1.10. In this humid region, the Riparian Doctrine requires a land owner to allow the stream to flow by or through his land in its natural state. Thus, in its strict sense, the right does not allow for the consumptive use of the water except for small domestic needs. When irrigation becomes necessary in a riparian state, the courts modify the doctrine to allow reasonable use in relation to neighboring users. No riparian user can take all the water of a stream and allow none to flow down to his neighbor. This contrasts sharply with the appropriator's right in other parts of the country to consume all that he needs. The Mountain States follow the Appropriation Doctrine exclusively; other states recognize both doctrines. In those states that recognize both, the relative importance of each doctrine varies considerably.

In addition to riparian and appropriation rights, there is a third kind of right based on need. Some examples of this type are Indian water rights, Federal Reserve rights, and, in some cases, municipal rights. These rights will be discussed later.

"In all states, water laws relating to ground waters generally are based on either the Riparian Doctrine or the Appropriation Doctrine. The Eastern States generally use the

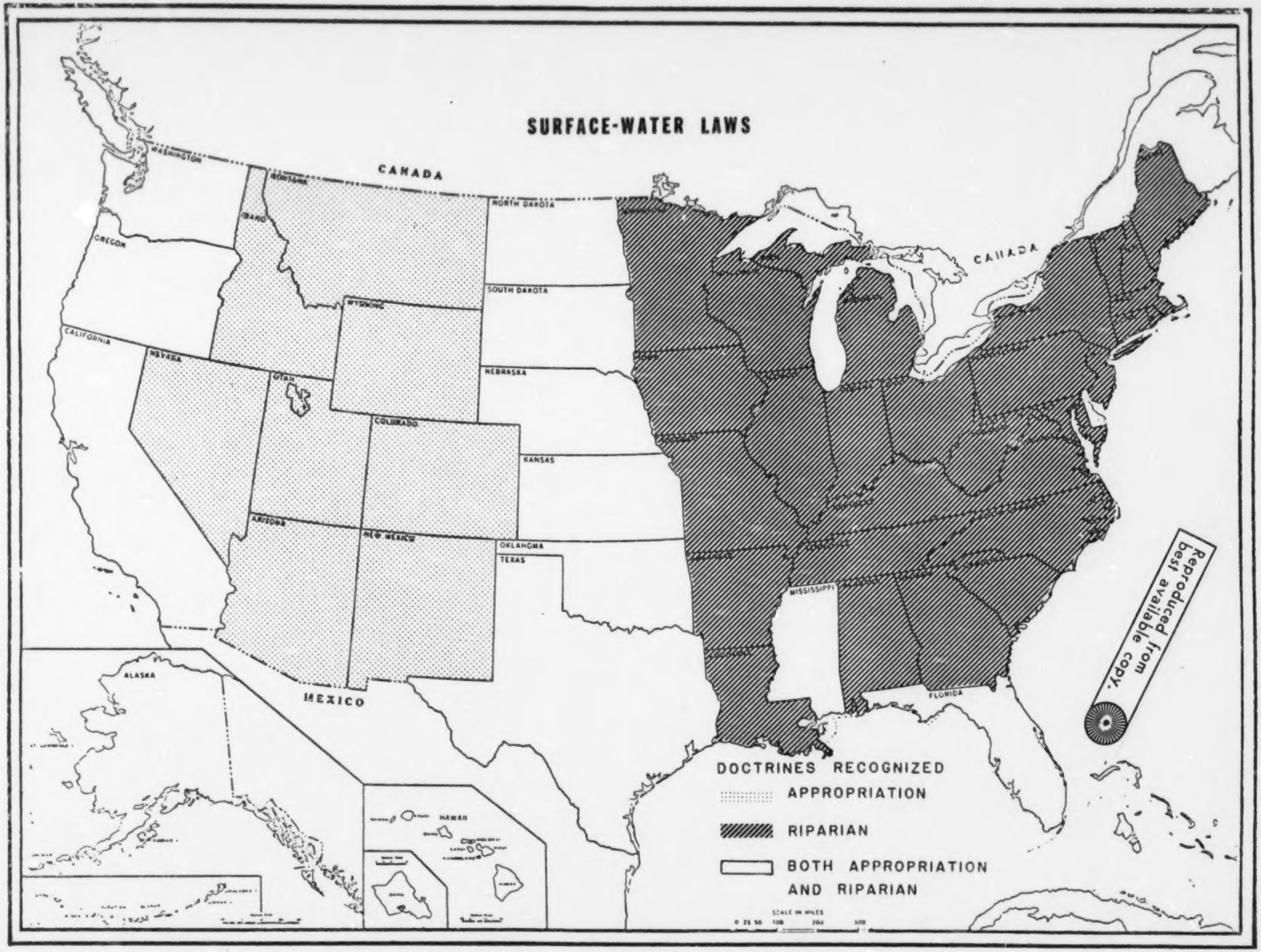
SURFACE-WATER LAWS
CANADA
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
COLORADO
ARIZONA
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MISSISSIPPI
FLORIDA
MEXICO
ALASKA
HAWAII
DOCTRINES RECOGNIZED
APPROPRIATION
RIPARIAN
BOTH APPROPRIATION AND RIPARIAN
SCALE IN MILES
0 25 50 100 200 300

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FIGURE B-1

English common-law version of the Riparian Doctrine, which gives absolute ownership of ground water to the land owner. Fifteen states modify this version and apply the American rule of 'reasonable use', which restricts the landowner's rights in relation to others. California goes one step further in the modification of the Riparian Doctrine with its doctrine of 'correlative rights'. Here, the landowner's use must not only be reasonable, but must be correlated with the uses of others during times of shortage. When the supply is limited, use is restricted to the lands directly overlying the common supply." The applicable ground water laws in the United States are shown on Figure B-2.

"While the Appropriation Doctrine seems to function easily for surface-water supplies in the arid states, it runs into some difficulty when it is applied to ground water. The main reason for this is that ground water is a hidden resource, whose occurrence and movement are poorly understood by most people.

Many states, in recent years, have begun to expand their control and regulation of ground-water use, and this has resulted in the creation of many special rules and regulations. Some of these apply to methods of well construction, monitoring of changes in ground-water levels and ground-water quality, periodic submission of data on ground-water use, and preventive measures to minimize contamination and pollution" (GE-058).

Federal Water Laws

The Federal Government was given limited powers relating to water resource development which are either expressly delegated or can be reasonably implied from the Constitution. There are a

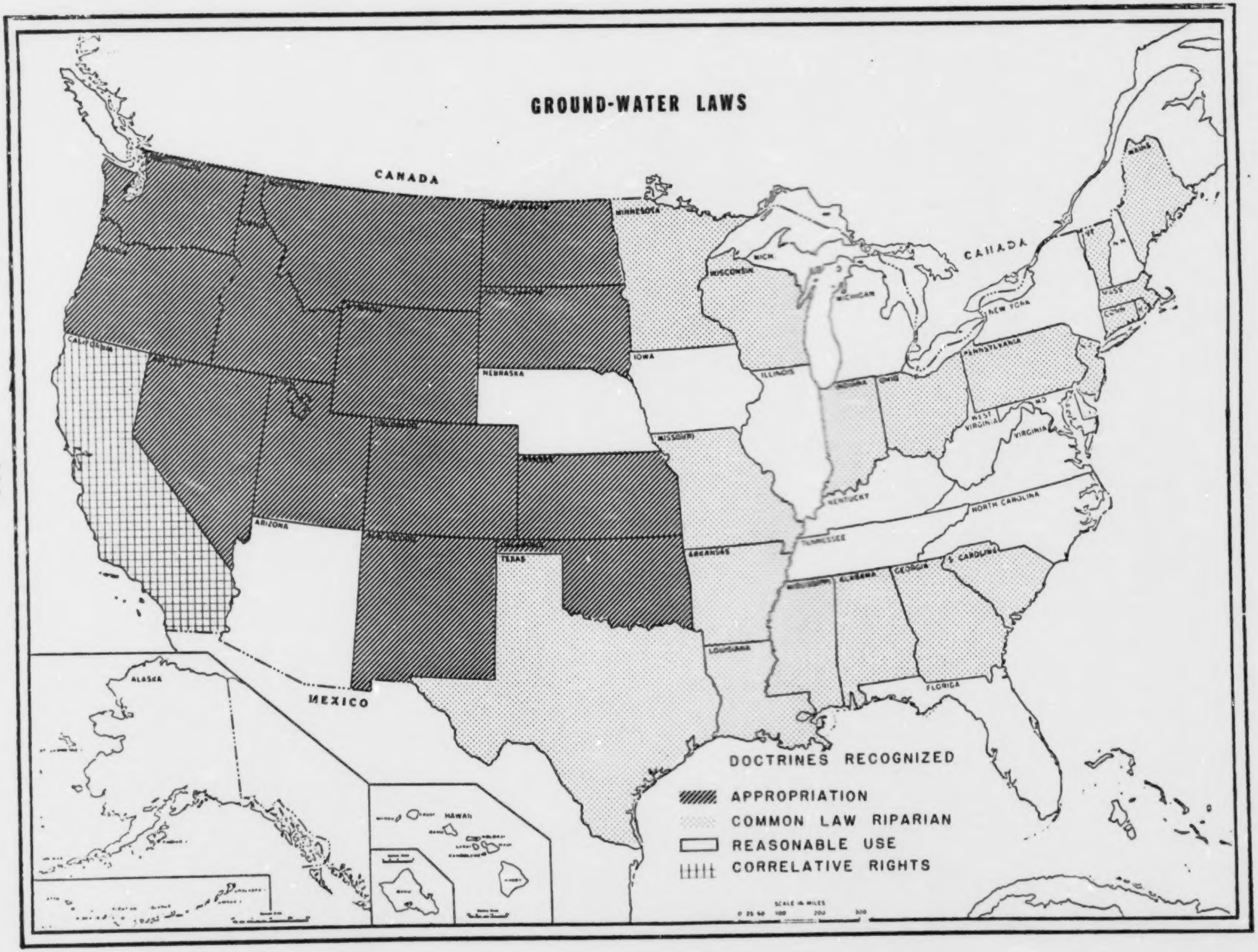

GROUND-WATER LAWS
CANADA
CANADA
MINNESOTA
NEBRASKA
IOWA
WISCONSIN
MICH
MICHIGAN
ILLINOIS
INDIANA
OHIO
NEW YORK
PENNSYLVANIA
MAINE
VT
NH
MASS
CONN
WEST VIRGINIA
VIRGINIA
MD
KENTUCKY
TENNESSEE
NORTH CAROLINA
S CAROLINA
GEORGIA
ALABAMA
MISSISSIPPI
FLORIDA
LOUISIANA
ARKANSAS
MISSOURI
KANSAS
TEXAS
ARIZONA
CALIFORNIA
MEXICO
ALASKA
HAWAII
DOCTRINES RECOGNIZED
APPROPRIATION
COMMON LAW RIPARIAN
REASONABLE USE
CORRELATIVE RIGHTS
SCALE IN MILES
0 25 50 100 200 300

FIGURE B-2

number of Federal laws that specifically effect the basins under consideration. Some of the more important laws are:

Indian Water Rights

Under a variety of treaties, acts, and executive orders enacted around the turn of the century, numerous Indian reservations were created in the central western states.

"Responsibility for the administration of Indian lands and waters on these reservations rests with the Bureau of Indian Affairs; however, the rights to the lands and water actually are vested with the Indians or tribes. The Indians of each reservation appear to have some legal claim to the use of the waters located on or flowing through or along its boundaries. Such rights are read from the treaties and agreements between the Indian tribes and the United States which have been approved by acts of Congress or formalized by Executive Orders. The Indian people claim a right to these waters free from State regulation and with a priority at least as early as the date the reservation was recognized or established. The Indian water right priority is not conditioned on use and may be exercised at any time. The Indian right can be quantified by fixing the amounts of water needed to serve the purpose or purposes for which the reservation was established. (See Winters v. United States, 207 U.S. 564 (1903); Conrad Investment Co. v. U.S. 161 Fed 829 (9th cir. 1908); U.S. v. Walker River Irrigation District 104 Fed 334 (9th cir. 1939); U.S. v. Ahtanum Irrigation District 235 Fed 321 (9th cir. 1956); and in closing, Arizona v. California 373; 546-600 (1963). Thus if the purpose were to promote an agricultural economy, as has been the case generally, the quantity of water reserved would be the amount needed to serve the practically irrigable acreage on the reservation. It also has been urged on behalf of the Indians that since the purpose of the Indian reservation is to provide an economic base for the Indian people residing thereon, it must follow that the Indian water right is a right to use the available reservation waters for any beneficial use including irrigation, livestock, domestic, power, recreation, industrial and municipal purposes. Nevertheless, several State water administrators continue to urge that the Indians are entitled only to that water for which proper application under State procedures has been made.

The irrigation of Indian lands was authorized by the General Allotment Act of February 8, 1887, which also provided that the Secretary of the Interior should make a just and equal distribution of the available water among the Indians. Later the Act of April 4, 1910, made specific provision for irrigation developments on Indian reservations, and special authorizations have been provided by Congress for many individual projects. The right to use Indian water for nonirrigation purposes has not been litigated or judically determined" (NO-055).

Mexican Water Treaty

"In the Mexican Water Treaty of 1944, Mexico is guaranteed an annual quantity of 1,500,000 a.f. of water from any and all sources. The water is to be delivered to that section of the river, away from any shores or bottom, near the international boundary" (NO-055).

Boulder Canyon Acts

The Boulder Canyon Project Act of December 21, 1928 approved the Colorado River compact of 1922 and provided for the construction of Hoover Dam and the All American Canal in the Lower Colorado Basin.

The Boulder Canyon Project Adjustment Act of July 19, 1940 (54 Stat. 774), among other things, provided funds for planning for the use of water in the states of the Upper Colorado Basin.

Other Acts of Interest

An excellent review of other Federal laws that effect the central western energy states is found in the Water Work Group Report of the Northern Great Plains Resource Program, pgs 29-42 (NO-055). These laws are broken down into the basic areas of interest in water resource development, including:

(1) Irrigation,

(2) Power,

(3) Navigation,

(4) Municipal and Industrial Water Supply,

(5) Flood Control,

(6) Watershed Protection and Flood Prevention,

(7) Outdoor Recreation, Fish and Wildlife,

(8) Environment,

(9) Water Quality, and

(10) Planning.

More detailed discussions of legal water-use constraints are also available in several of the other references cited in the bibliography (US-168, NA-190, NA-176).

APPENDIX 6.1-4

ATMOSPHERIC STABILITY CLASSES AND PLUME DISPERSION CHARACTERISTICS

The dispersive characteristics of the planetary boundary layer (the lowest 3000 to 4000 feet of the troposphere) are primarily a function of the mean motion of the atmosphere and fluctuations or turbulence about the mean motion. The turbulence is to a great extent a function of the stability or temperature lapse rate of the boundary layer. Stability can be divided into six classes for purposes of the dispersion modeling of pollutants. These classes, based on EPA's Climatological Dispersion Model (CDM) are:

Stability Class	Description
A	Extremely unstable
B	Moderately unstable
C	Slightly unstable
D (day)	Neutral (daytime)
D (night)	Neutral to slightly stable (nighttime)
E + F	Stable to extremely stable

This classification scheme, developed by Pasquill and Gifford, has associated with it a set of coefficients of diffusion, both in the horizontal and the vertical. That is, each stability class has a diffusivity associated with it. As the air becomes more stable its diffusive capabilities decrease.

A consideration of the individual stability classes as defined by Pasquill and their effects on pollutant dispersion can now be conducted. Under the CDM scheme, the unstable classes are A, B, and C. D (day) is the classification when the lapse rate is neutral during the day. The four stability classes listed above can occur only during the daylight hours.

The occurrence of Classes D (night) and E + F is confined to the nighttime hours. D (night) stability occurs during cloudy and/or very windy nights, when vertical mixing is sufficient to prevent the formation of very stable lapse rates or ground-based inversions. E + F stability is confined to those nights with surface winds of 9 knots or less and clear or scattered sky/cloud conditions.

Stability Class A occurs very rarely, usually with a relative frequency of occurrence of 2% or less on an annual basis. For such a stability regime to occur, skies must be clear, the sun must be nearly overhead, and winds must be 5 knots or less. In such a situation, the lapse rate is very unstable, much greater than the dry adiabatic rate. Thermals are numerous and vertical mixing and turbulence are extreme. In such a case, a plume emitted from a stack will have a large plume rise and, therefore, a large effective stack height. However, the plume will not be dispersed rapidly because of the light winds. In addition, the large coefficient of vertical diffusion due to strong vertical mixing causes the plume to expand rapidly in the vertical so that high pollutant concentrations reach the ground within a very short distance from the stack. Since the plume trajectory in such a situation does not follow a long path, there is not sufficient air flow to allow for dispersion and dilution of the plume. Therefore, high ground level pollutant concentrations can occur during a short-term sampling period under these meteorological conditions.

When a plume from a stack is dispersing under very unstable conditions, such as A or B stability, it exhibits a phenomenon known as looping (Figure 1). In addition to diffusing rapidly in the vertical because of forced mixing from the instability of the air, the plume exhibits a variety of shapes and sizes because of the thermal currents. As a result, the plume "loops" (from plume classification scheme by Church) causing alternately high and low ground-level pollutant concentrations as the pollutants travel along the plume trajectory. In such a case, the pollutant concentration measurements would have a high standard deviation. Even though the pollutant concentration varies rapidly under looping conditions, a time averaging process can be used to obtain an average concentration over a short time interval of about 30 minutes to 1 hour.

B and C stabilities cause the plume to behave in much the same manner as it does with A stability, except that the plume does not diffuse in the vertical as rapidly as it does with A stability. With B and C stabilities, therefore, the plume touchdown is further downwind than with A stability, thus affording more dispersion and diffusion along the plume trajectory to touchdown. Lower ground-level concentrations are the result.

Under unstable lapse rate conditions, the stronger the winds, the lower the plume rise and the higher the ground-level pollutant concentrations.

When the lapse rate is neutral such as with D (day) and D (night) stabilities, the plume does not diffuse appreciably, resulting in "coning" (Figure 2). If E + F stability prevails, diffusion is minimal in both a lateral and vertical sense. Therefore, the plume remains rather concentrated and advects for great distances before reaching the ground (Figure 3).

Two other plume configurations are shown in Figures 4 and 5. Figure 4 is characteristic of nocturnal radiation conditions, in which a shallow ground-based inversion is formed.

The air above is neutral. Therefore, the plume only disperses in an upward direction since the air below is very stable and will not mix. The result is "lofting".

Figure 5 illustrates the phenomenon known as "fumigation" or inversion breakup. Such a condition occurs when a vertical temperature distribution such as Figure 3 or Figure 4 is modified by heating of the ground during the morning. As a result, the lowest layer of air becomes very unstable causing pollutants which had been suspended aloft to diffuse rapidly to the ground.

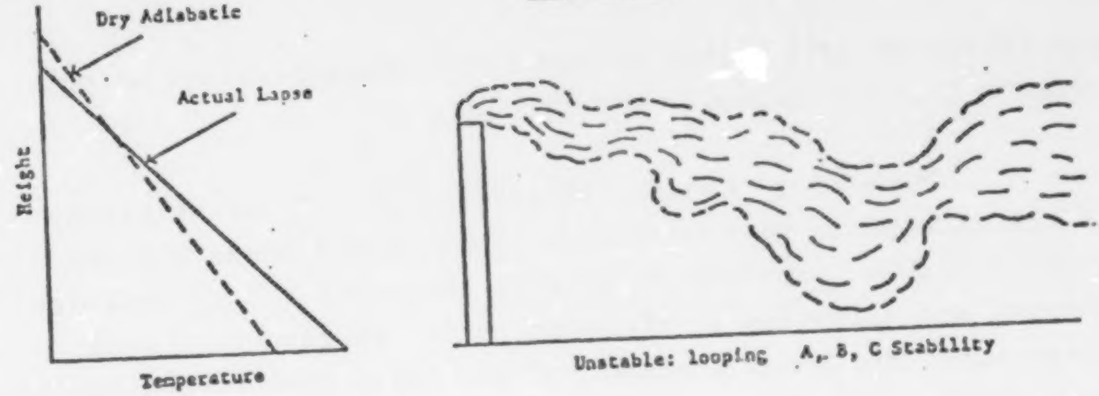
A troublesome aspect of stability assessment is the fact that the lower portions of the planetary boundary layer often have multiple stratifications of stability. That is, the stability of the air varies drastically with small increments of increasing height above the surface. On many occasions, superadiabatic ("A" stability) layers or strong inversion layers ("E + F" stability) are confined to approximately the lowest 100 feet of the atmosphere. Above this layer the air may stabilize or destabilize rapidly with increasing height. If stability varies considerably with height, attempts to classify the stability of the planetary boundary layer into one classification independent of height based on low-level stability determinations yield stability classifications that misrepresent the true state of the atmosphere.

Such stability classifications independent of height can also cause erroneous results in dispersion modeling efforts. Distributions of stability measurements taken in the lowest 100 feet of the boundary layer will be skewed toward the unstable end of the classification spectrum because of the introduction of components of surface heating and mechanically-induced turbulence into the raw data. Such a stability distribution, if used in dispersion modeling of tall stacks, could result in the prediction of much higher ground-level concentrations of pollutants than are actually experienced.

The effect that the stratification of the stability of the atmosphere will have on a plume of emissions will be quite variable. Factors which will influence the general dispersion and diffusion of the plume are: surface roughness parameters, depth and gradient of the lapse rate stratifications, wind speed, wind shear, and net radiation. A "looping" plume may "cone" in some locations and vice versa.

In summary, the ground-level concentrations of pollutants which are experienced during a short period of time are a function of the stability of the air and the wind speed. Stability classifications simply indicate the change of temperature with increasing height. If air temperatures decrease rapidly with height, the air is unstable. If the air cools only moderately with height, it is neutral. If the air warms with height, it is stable.

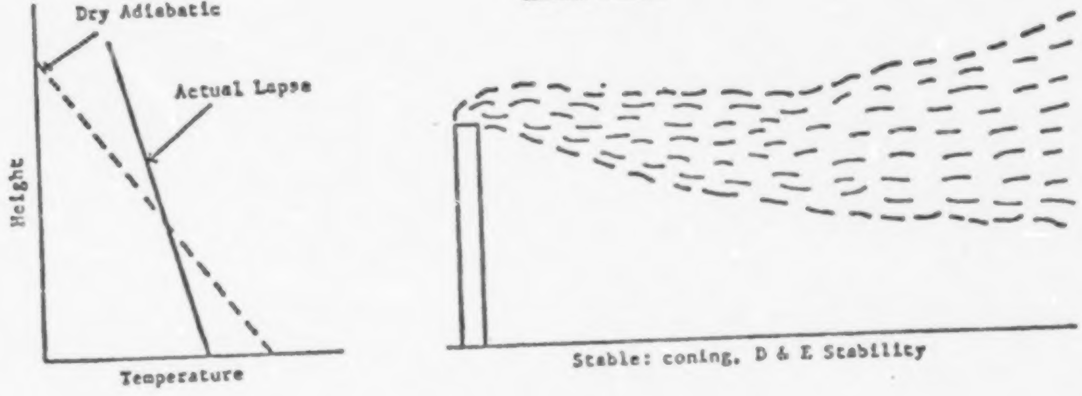
Figure 1


Dry Adiabatic
Actual Lapse
Height
Temperature

Unstable: looping A, B, C Stability

This condition is associated with unstable conditions, since the air cools rapidly with height. The plume exhibits this "looping" behavior when "A", "B", or "C" stability conditions exist. Plume touchdown is relatively close to the source.

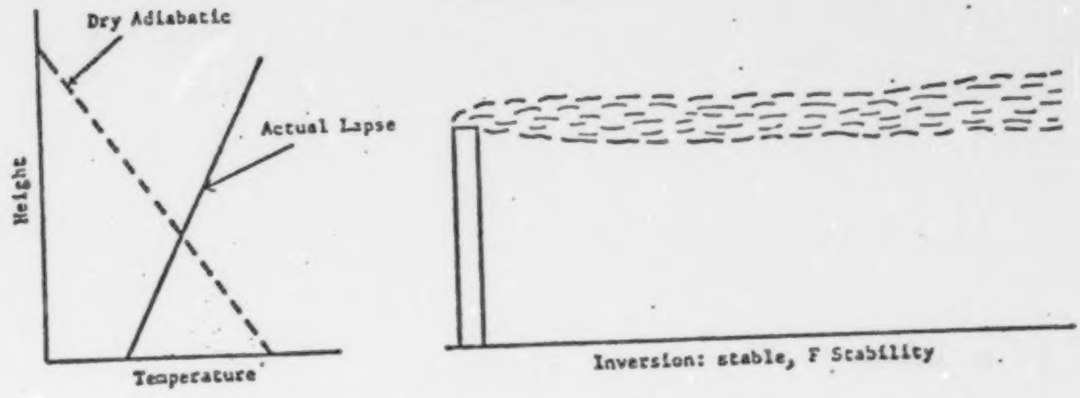
Figure 2


Dry Adiabatic
Actual Lapse
Height
Temperature

Stable: coning, D & E Stability

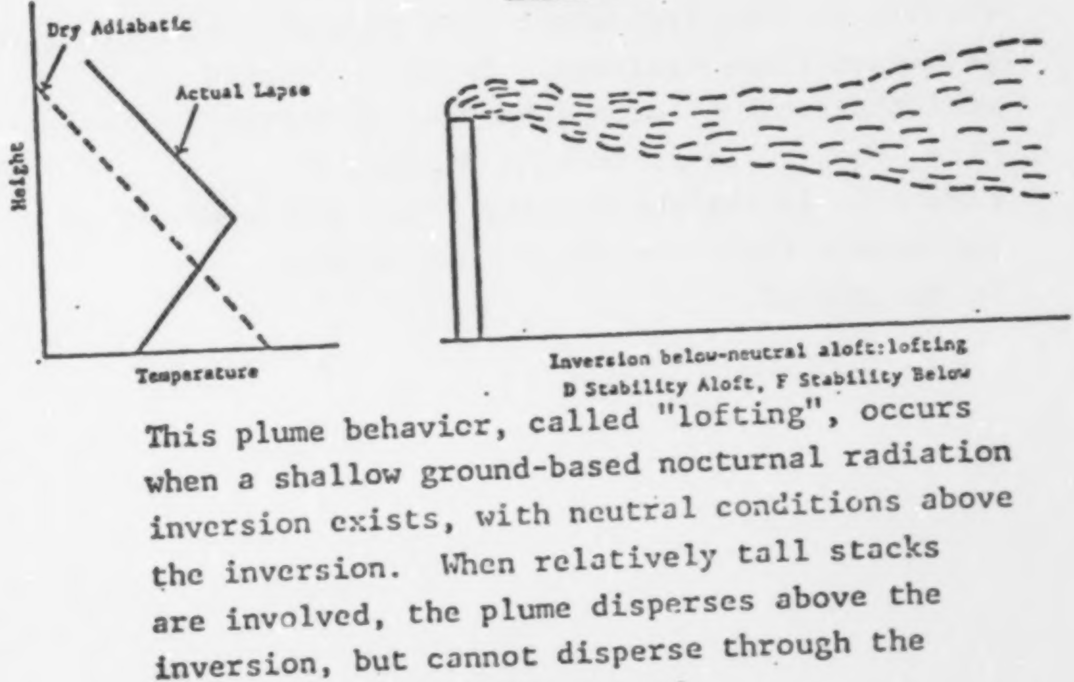
This plume behavior, called "coning", occurs when neutral or slightly stable conditions such as D (day) or D (night) stability exist. The plume generally travels farther before it reaches the ground than in the unstable cases.

Figure 3


Dry Adiabatic
Actual Lapse
Height
Temperature
Inversion: stable, F Stability

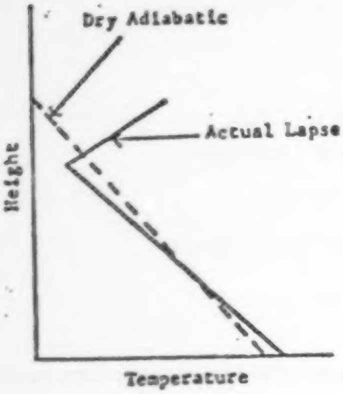
This plume behavior, called "fanning", occurs during "E + F" stability, when the air is very stable, such as when an inversion is present. The plume travels a great distance in an essentially undiluted state before it reaches the ground.

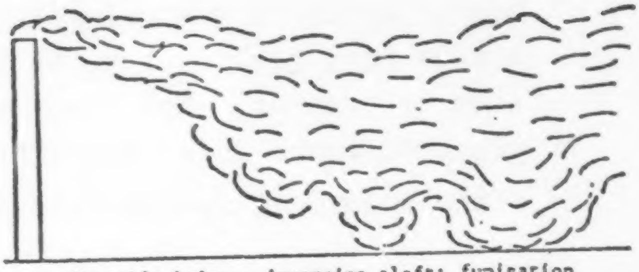
Figure 4


Dry Adiabatic
Actual Lapse
Height
Temperature
Inversion below-neutral aloft:lofting
D Stability Aloft, F Stability Below

This plume behavior, called "lofting", occurs when a shallow ground-based nocturnal radiation inversion exists, with neutral conditions above the inversion. When relatively tall stacks are involved, the plume disperses above the inversion, but cannot disperse through the inversion to reach the ground.

Figure 5




Unstable below - inversion aloft: fumigation

This condition, called "fumigation", often results in very high short-term ground-level pollutant concentrations. It is associated with the break-up of a ground-based inversion, such as is present in Figure 3 or Figure 4, during the morning. The undiluted pollutants aloft are rapidly mixed down to the ground.

APPENDIX 6.1-5

ATMOSPHERIC DISPERSION MODELS

Radian uses three different models to calculate air quality levels depending on the averaging time associated with a particular Federal or state standard. Each of the three models uses the same plant emissions data and standard Gaussian dispersion relations, but the detailed treatment of the meteorological variables differs among the various models.

The three models used are a long-term average model, a short-term model, and a 24-hour average model.

The long-term average model uses historical meteorological data to estimate annual average pollutant concentrations. These estimated annual averages can also be used in conjunction with certain statistical assumptions to estimate maximum concentrations for averaging times less than one year (e.g. monthly). The short-term model computes estimated concentrations corresponding to a 10-minute averaging time. A statistical assumption, different from that employed in the annual average model, is used to transform the 10-minute average estimates to estimates corresponding to other averaging times (usually 3 hours or less).

The long-term model is used to estimate concentrations for averaging times greater than three hours. The short-term model is used to estimate concentrations for averaging times less than three hours.

The long-term model is similar to the Climatological Dispersion Model (CDM) recently developed at the National Environmental Research Center, Research Triangle Park, North Carolina. The CDM is a long-term average model which utilizes long-term meteorological data in conjunction with Gaussian dispersion using Pasquill-Gifford dispersion coefficients. This model is essentially an updated version of the well-known AQDM (Air Quality Display Model) developed under EPA auspices and both models share a common conceptual approach. The primary differences between the two models relate to calculation of plume rise for point sources, specification of mixing heights and wind profiles, and the treatment of the effects of area sources.

The average concentration $\bar{C}_A$ due to area sources at a particular receptor is given by

$$\bar{C}_A = \frac{16}{2\pi} \int_0^\infty \left[\sum_{k=1}^{16} q_k(\rho) \sum_{\ell=1}^{6} \sum_{m=1}^{6} \Phi(k,\ell,m) \; S(\rho, z, u_\ell, P_m) \right] d\rho \qquad (1)$$

where

k = index identifying wind direction sector

$q_k(\rho) = \int Q(\rho,\phi)\, d\phi$ (k sector)

$Q(\rho,\phi)$ = emission rate of the area source per unit area and unit time

ρ = distance from the receptor to an infinitesimal area source

ϕ = angle relative to polar coordinates centered on the receptor

ℓ = index identifying the wind speed class

m = index identifying the class of the Pasquill stability category

$\Phi(k,\ell,m)$ = joint frequency function (generally for an annual period)

$S(\rho,z,u_\ell,P_m)$ = dispersion function defined in Equation 1

z = height of receptor above ground level

u_ℓ = representative wind speed

P_m = Pasquill stability category

For point sources, the average concentration $\bar{C}p$ due to N point sources is given by

$$\bar{C}_P = \frac{16}{2\pi} \sum_{n=1}^{N} \sum_{\ell=1}^{6} \sum_{m=1}^{6} \frac{\Phi(k_n,\ell,m)\ G_n\ S(\rho_n,z,u_\ell P_m)}{\rho_n} \qquad (2)$$

The total concentration for the averaging period is the sum of concentrations of the point and area sources for that averaging period.

For point sources, the effective stack height, h, is the sum of the physical stack, h_o, and the plume rise, Δh:

$$h = h_o + \Delta h \qquad (3)$$

The plume rise, Δh, is computed with formulas developed by Briggs. For unstable and neutral conditions:

$$\Delta h = 1.6F^{1/3} \; U^{-1} \rho^{2/3} \qquad \rho \le 3.5X^* \qquad (4)$$

and

$$\Delta h = 1.6F^{1/3} \; U^{-1}(3.5X^*)^{2/3} \qquad \rho > 3.5X^* \qquad (5)$$

$$X^* = 14F^{5/6} \quad \text{if } F \le 55$$

$$X^* = 34F^{2/5} \quad \text{if } F > 55$$

$$F = g \; V_s \; R_s^2\{(T_s - T_a)/T_s\}$$

where

g = acceleration due to gravity

V_s = average exit velocity of gases of plume

R_s = inner radius of stack

T_s = average temperature of gases of plume

T_a = ambient air temperature

U = wind speed

ρ = distance from source to receptor

For stable conditions

$$\Delta h = 2.9\ (F/Us)^{1/3} \qquad \rho > 2.4\ Us^{-\frac{1}{2}} \tag{6}$$

(i.e., Equation (6) rather than Equation (4) or (5) is used for stable conditions)

where

$$s = \frac{g}{T_a}\ \frac{\partial \theta}{\partial z} \tag{7}$$

θ = ambient potential temperature

z = height.

The short-term model employed is similar to the long-term model in that the Briggs Plume Rise Formulas and the Pasquill-Gifford dispersion formula are employed. Specifically the ten-minute average concentration due to N point sources is computed from

$$\overline{C}_p = \frac{1}{\pi} \sum_{n=1}^{N} G_n\ P(x,y,o;u_\ell,P_m) \tag{8}$$

where

x = downwind distance

y = crosswind distance

$$P(x,y,o;u_\ell,P_m) = \frac{1}{\sigma_y(x)\sigma_z(x)u_\ell} \exp\left[-\frac{1}{2}\left(\frac{h}{\sigma_z(x)}\right)^2\right] \quad (9)$$

$$\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y(x)}\right)^2\right]$$

$\sigma_y(x)$ = the horizontal dispersion function and the rest of the symbols have been previously defined.

Equation (9) corresponds to a ten-minute averaging time because the σ_z's are experimentally determined for a ten-minute averaging time. Short-term area source calculations are made by integrating an equation similar to Equation (9) over each area.

The concentration for averaging times other than ten minutes are computed from the relation

$$X_s = X_k\left(\frac{t_k}{t_s}\right)^{0.2} \quad (10)$$

where X_s is the desired concentration estimate for the sampling time, t_s; and X_k is the concentration estimate for the sampling time t_k.

The joint probability function $\phi^{(k,\ell,m)}$ is obtained from historic meteorological data collected at meteorological stations near the site in question. Average ambient temperature and average daytime and nighttime mixing height for each site are obtained from an analysis of the meteorological data for the site.

Because of the uncertainty associated with the log-normal statistical extrapolation procedure previously referred to in connection with scaling annual values back to shorter averaging times, which becomes larger as the procedure is applied to shorter averaging times, Radian has felt it desirable to augment the two models described by a 24-hour average model. This model might be considered as a hybrid of the two models previously described in the sense that it incorporates some of the averaging features of the long-term model with the statistical assumptions of the short-term model.

In essence, the model is based on a recognition of the fact that during a 24-hour period meteorological conditions and plant conditions will change with time sufficiently to invalidate the two-tenths power scaling rule applied over a 24-hour period. On the other hand, over such a period of time the assumption that conditions will change according to an annual frequency distribution is also not realistic. Consequently the 24-hour period is assumed to be divided into an integral number of shorter time intervals with specified plant emissions and meteorological conditions which are assumed constant within a time interval, but which can change from interval to interval. For a given interval, the short-term model using the two-tenths scaling rule is used to compute the concentration at a particular receptor for the interval, and the final 24-hour concentration is computed as a uniformly weighted average of the contributions from the individual time intervals.

7.0 AREAS FOR RESEARCH AND DEVELOPMENT

The evaluation of the environmental aspects of the oil refining, LNG, and liquid-based SNG industries leads to the identification of several areas of research and development needs. These are itemized below.

Ambient Air Monitoring

There is a real need for an automated field hydrocarbon monitor which will provide a detailed breakdown of the hydrocarbon species. This would provide an excellent clue to their sources, and thus greatly simplify the control of such emissions. Fugitive hydrocarbon emissions are a serious problem as has been discussed earlier. Given information on species and ratios between various species, along with compositions of the various process streams, "fingerprinting" techniques could be developed to greatly localize the source of fugitive emissions.

Pollutant Dispersion

Better methods of tracing pollutants in the atmosphere are needed. With a wide number of easily detectable tracers, the contributions of many local sources to the air quality in an area could be determined and allow the optimum control strategy to be developed.

There also is a real need for an air monitoring rationale, i.e., how many stations should be used, how should they be sited, should they be moved seasonally, etc. It is presently difficult to compare results from various networks due to uncertainties resulting from the network designs.

These needs are inter-related to the need for better prediction from diffusion models. The data obtained identifying sources with ambient concentrations is needed to "tune" developing sophisticated models. The "tuned" models in turn would be of great value in establishing air monitoring network designs.

Effects

Additional data is also needed regarding the fate of pollutants in the environment and their long-term effects on plant and animal life. In particular, the effects of hydrocarbons and NO_x, separately and jointly, need to be better understood. If additional information could be obtained regarding the role of various hydrocarbon species or classes of hydrocarbon species in the formation of photochemical smog, more realistic ambient air hydrocarbon standards could be developed. This would allow the expenditures for controls to be channeled to the most effective areas.

Water Monitoring

There is a need for automated field analyzers to detect all the parameters for which emission limits have been set for petroleum refineries. Reliable automated analyzers would greatly reduce man-power requirements in demonstrating compliance with the regulations. Also automated data acquisition systems to provide summary reports and trigger alarms are needed.

Water Effluent Control

The provisions of the Clean Water Act require zero discharge or zero impact in future years. Development work is needed in determination of the applicability of such technologies as ion exchange, membrane separation processes, and forced evaporation processes to refinery effluent streams.

Cost Impacts

Studies are needed to indicate trends in plant costs as functions of increased emissions controls and improved fuel economy. Because of increasing energy costs, the trends in new plant designs are moving toward greater fuel utilization. This has the secondary effects of reducing total emissions and total cooling water requirements.

While energy conservation is in itself a desirable feature, concurrent cost savings can in some cases cover the expense of added control equipment. Engineering studies of the various cost alternatives are needed.

"Negative" Thermal Pollution Control

LNG regasification plants' water discharge is a few degrees colder than the temperature of the receiving water. This is a form of a "negative" thermal pollution. This pollution will affect the life cycle of the marine organisms near the outfall. The subject of "negative" thermal pollution has been overshadowed by the "positive" thermal pollution. As a result, less information has been collected regarding its environmental impact. Some effort should be made to develop schemes and design criteria for control of "negative" thermal pollution. The study must investigate its adverse effects on the environment and the cost of controlling it.

Solid Wastes

The chemical composition of typical solid wastes from refineries should be examined in detail to determine the content of hazardous or potentially hazardous species. The solubility of these species should be determined, and the long term chemical stability-solubility of these materials in a landfill environment should be studied.

The movement and attenuation of any soluble hazardous species in various types of soils should be examined. Also, the long term stability in the landfill environment of liners for disposal sites should be examined.

Hazardous Chemicals

A comprehensive and cost effective sampling and analytical strategy is needed for plant effluent streams. The objective of this effort would be to provide a means of detecting potentially hazardous materials in these effluents. Field testing to verify these strategies will also be needed.

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